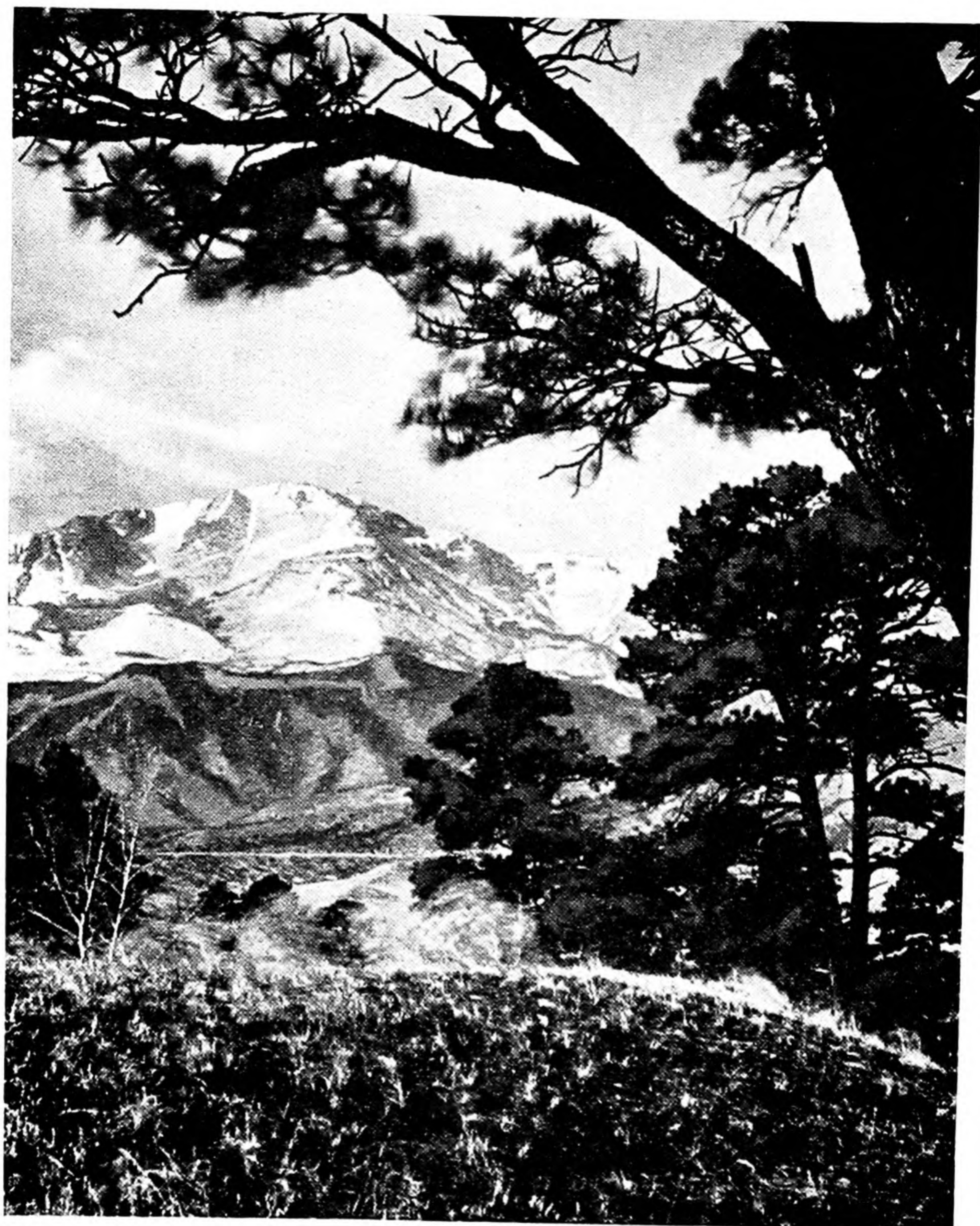




# CHEMICAL CONTROL OF INSECTS





**Fig. 1.**—A view from Colorado Spring, where the Colorado beetle obtained its name. *Photograph by courtesy of Findon Publications.*

*Frontispiece*



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# CHEMICAL CONTROL OF INSECTS

by

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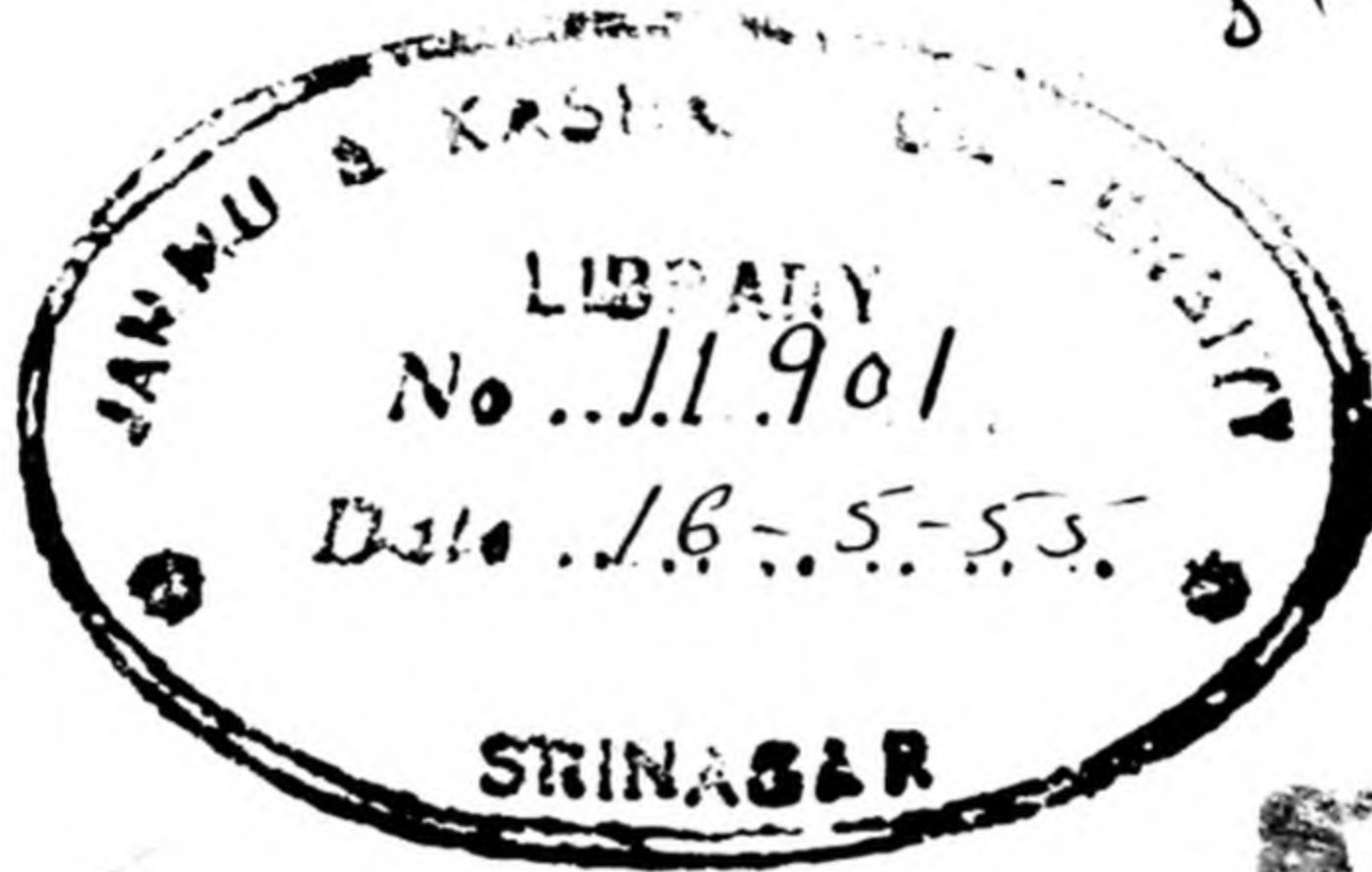
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## PREFACE

IN these days of intensive and extensive research there may be a tendency for a worker in one field to receive a blurred and even partially inaccurate impression of the scope of advances in other fields.

This was brought home in connection with the development of the use of D.D.T. during the war and it is unfortunate that in some sections of the Press the facts should have received such scant consideration.

In this book we have endeavoured to provide a survey of the main insecticides emphasizing the more modern developments.

Some of the insecticides still widely utilized to-day were discovered as possessing insecticidal properties many years ago—the capacity of pyrethrum flowers to kill insects was recognized, for instance, at the beginning of the nineteenth century. Whilst accounts of the circumstances of this discovery vary it is almost certain that the observation was an accidental one. On the other hand, the recent discovery of the insecticidal properties of D.D.T. followed a prolonged and well-planned research effort. The importance to mankind of insecticides in controlling insect vectors of diseases such as typhus and malaria and in controlling insect pests on plants is too well known to require emphasis. However, in the glamorous aspect of chance observation and equally in the romantic success story of long-term effort, the chemistry of insecticides seems to reflect in vivid outline an aspect of scientific development of which we are apt to lose sight in these days of pre-occupation with the dire possibilities to man of various recent advances in science.

We have attempted to compare and contrast the methods of using the main insecticides in addition to considering briefly the chemistry of the various substances and hope that the impetus given to the investigation of insecticides by exigencies of the war and an idea of the present field of endeavour has been indicated. The chapter on chlorinated hydrocarbons, for instance, will indicate that the possibilities for new synthetic compounds even in this limited field are by no means exhausted. No synthetic chemical available and suitable for the purpose

## PREFACE

exhibits, at anything like equivalent concentrations, the "knockdown" properties to insects of that complex mixture of compounds known as the pyrethrins.

We are indebted to the editor of *Chemistry and Industry* for permission to quote extensively from papers by one of the authors (T.F.W.) published in that journal and to Dr. R. S. Cahn for his kindness in reading the manuscript on rotenone.

T.F.W.  
J.E.H.  
J.H.F.



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## ABBREVIATIONS OF REFERENCES

Ag. Chemicals	=	Agricultural Chemicals.
Amer. Ent.	=	American Entomologist.
Ann. App. Biol.	=	Annals of Applied Biology.
Ann. des Epiphytes	=	Annales des Epiphytes.
Ann. Rep. Agric. Hort. Res. Sta. Long Ashton	=	The Annual Report of the Agricultural and Horticultural Research Station, Long Ashton.
Australian Council Sci. Ind. Res.	=	Australian Council for Scientific and Industrial Research.
Ber.	=	Berichte der deutschen chemischen Gesellschaft.
Biol. Bull.	=	Biological Bulletin.
Biol. Section, H.S. Dept. T.V.A, Ala.	=	Biological Section, Health and Safety Department, Tennessee Valley Authority, Alabama.
Brit. Med. Bull.	=	British Medical Bulletin.
Brit. Med. J.	=	British Medical Journal.
B.P.	=	British Patent.
Bull. Entomol. Res.	=	Bulletin of Entomological Research.
Bull. Imp. Inst.	=	Bulletin of the Imperial Institute.
Bull. N.J. Agric. Exp. Sta.	=	Bulletin of the New Jersey Agricultural Experimental Station.
Bull. U.S. Army Med. Dep.	=	Bulletin of the United States Army Medical Department.
Bull. Wash. Agric. Exp. Sta.	=	Bulletin of the Washington Agricultural Experimental Station.
Calif. Agr. Exp. Sta.	=	California Agricultural Experimental Station.
Calif. Bull.	=	California Bulletin.
Calif. Citrograph	=	California Citrograph.
Ch. Abs.	=	Chemical Abstracts.
Chem. and Ind.	=	Chemistry and Industry.
Chem. Met. Eng.	=	Chemical and Metallurgical Engineering.
Conn. Agric. Exp. Sta. Bull.	=	Connecticut Agricultural Experimental Station Bulletin.
Cont. Boyce Thompson Inst.	=	Contributions of the Boyce Thompson Institute.
C.R. Soc. Biol.	=	Comptes Rendues Société Biologie, Paris.
Helv. Chim. Acta.	=	Helvetica Chimica Acta.
Hort. Ed. Ass. Year Book	=	Horticulture Education Association Year Book.
Imp. Bur. Ent.	=	Imperial Bureau of Entomology.
Ind. Eng. Chem.	=	Industrial and Engineering Chemistry.
Ind. Eng. Chem. (Anal.)	=	Industrial and Engineering Chemistry, Analytical Edition.
Iowa State College J. Sci.	=	Iowa State College Journal of Science.



## ABBREVIATIONS OF REFERENCES

J. Agric. Res.	=	Journal of Agricultural Research.
J. Agric. Sci.	=	Journal of Agricultural Science.
J. Amer. Chem. Soc.	=	Journal of the American Chemical Society.
J. Amer. Pharm. Assoc.	=	Journal of the American Pharmaceutical Society.
J. Assoc. Official Agr. Chem.	=	Journal of the Association of Official Agricultural Chemists.
J. Biol. Chem.	=	Journal of Biological Chemistry.
J. Chem. Soc.	=	Journal of the Chemical Society.
J. Econ. Ent.	=	Journal of Economic Entomology.
J. Oil Chem. Assoc.	=	Journal of the Oil and Colour Chemists' Association.
J. Min. Agric.	=	Journal of the Ministry of Agriculture and Fisheries.
J. Nat. Malaria Soc.	=	Journal of the National Malaria Society.
J. Org. Chem.	=	Journal of Organic Chemistry.
J. Proc. Australia Chem. Inst.	=	Journal of Proceedings of the Australian Chemical Institute.
J. Roy. Hort. Soc.	=	Journal of the Royal Horticultural Society.
J. R. Soc. Arts	=	Journal of the Royal Society of Arts.
J. Soc. Chem. Ind.	=	Journal of the Society of Chemistry and Industry.
Mich. Exp. St. Tech. Bull.	=	Michigan Experimental Station Technical Bulletin.
New Hampshire Agric. Exp. Sta. Bull.	=	New Hampshire Agricultural Experimental Station Bulletin.
N. J. Agric. Exp. Sta.	=	New Jersey Agricultural Experimental Station.
New York Agric. Exp. Sta. Bull.	=	New York Agricultural Experimental Station Bulletin.
New York State Agric. Exp. Sta.	=	New York State Agricultural Experimental Station.
N.Y. State Flower Growers' Inc. Bull.	=	New York State Flower Growers' Inc. Bulletin.
New Zealand J. Sci. Tech.	=	New Zealand Journal of Science and Technology.
Pharm. J.	=	Pharmaceutical Journal.
Plant Physiol.	=	Plant Physiology.
Proc. Ent. Soc. Wash.	=	Proceedings of the Entomological Society of Washington.
Proc. Helmin. Soc.	=	Proceedings of the Helminthological Society.
R.A.E.	=	Review of Applied Entomology.
Rep. Exp. Res. Sta. Cheshunt	=	Report of the Experimental Station, Cheshunt.
Rep. Mass. St. Bd. Agric.	=	Report of the Massachusetts State Board of Agriculture.
Rec. trav. chim.	=	Recueil des travaux chimiques des Pays Bas.
Schweiz Med. Woch.	=	Schweizerische Medizinische Wochenschrift.
Schweiz. Ztschr. f. obst. u. Weiz.	=	Schweizerische Zeitschrift für obst-und Weinbau.

## ABBREVIATIONS OF REFERENCES

Tech. Bull. Minnesota Agric. Exp. Sta.	=	Technical Bulletin of the Minnesota Agricultural Experimental Station.
Trans. Ent. Soc. London	=	Transactions of the Entomological Society, London.
Trans. Faraday Soc.	=	Transactions of the Faraday Society.
Trans. R. Soc. Trop. Med. Hyg.	=	Transactions of the Royal Society of Tropical Medicine and Hygiene.
U.S.D.A.	=	United States Department of Agriculture.
U.S.D.A. Bull.	=	United States Department of Agriculture Bulletin.
U.S.D.A. Bur. Ent. Plant Quarant.	=	United States Department of Agriculture, Bureau of Entomology and Plant Quarantine.
U.S.D.A. Comm. Agr. Rpt.	=	United States Department of Agriculture, Commercial Agricultural Report.
U.S.P.	=	United States Patent.
Univ. Illinois Agric. Exp. Sta. Bull.	=	University of Illinois Agricultural Experimental Station Bulletin.
Univ. Minnesota Agric. Exp. Sta. Tech. Bull.	=	University of Minnesota Agricultural Experimental Station Technical Bulletin.
Univ. Tennessee Agric. Exp. Sta. Bull.	=	University of Tennessee Agricultural Experimental Station Bulletin.
Vest. Kral. Česke Společnosti, Nauk.	=	Věstník Královské České Společnosti Nauk.

## ABBREVIATIONS

D.N.C.	=	Dinitrocresol	kg.	=	kilogram or kilograms.
DNOC.	=	Dinitro <i>ortho</i> cresol	lb.	=	pounds
ft.	=	feet	m.	=	metre
g.	=	gram or grams	ml.	=	millilitre or millilitres
gal.	=	gallon	mol.	=	molecule
gals.	=	gallons	oz.	=	ounce
gal. (U.S.)	=	United States gallon	p.p.m.	=	parts per million
gals. (U.S.)	=	United States gallons	sq.	=	square





## CHAPTER I

### INTRODUCTION

ALTHOUGH this book is concerned primarily with the destruction of insects by chemical methods, we thought it advisable to include some reference to the use of repellents and attractants in view of the tremendous revival of interest in repellents during the war. The importance of repellents in preventing attack by insects carrying diseases is clearly of the greatest importance—ignoring the prevention of annoyance caused by mosquitoes and “gnats” when a health hazard is not involved. In agriculture, also, the grower is interested in any material which can assist in protecting crops from attack until harvest-time. For instance, the control of Japanese beetle (which attacks about 250 kinds of plants, shrubs and flowers) is sometimes attempted by using insecticides or substances which prevent attack. The use of attractant substances in traps and baits is well known, for instance, flies are known to be attracted by the addition of small amounts of formaldehyde to milk.<sup>1</sup> The new insecticide “Gammexane” (trade name of the  $\gamma$ -isomer of benzene hexachloride) has been used<sup>2</sup> in attractive bran baits with considerable success against crickets and locusts.

For similar reasons we have also given a brief account of the newer growth regulators (Chapter XVI)—a subject which comes very much into the purview of the practical entomologist since the elimination of weeds as alternative host plants for insect pests is of considerable interest.

#### Methods of use

Insecticides are rarely employed in the pure state. The active principle is usually combined with an inert diluent such as talc to form a dust or with inert fillers and wetting and suspending agents and applied as a suspension or as a constituent of an emulsion. Other methods include the use of a gas or a smoke as a fumigant and during the war the use of aerosols was developed.\*

\* See page 136



The discovery of compounds possessing strong residual action has permitted the use of these insecticides in suitable paints and as proofing agents by impregnating fabrics and clothing.

Whilst it appeared convenient to follow the classical precedent of dividing the book into two sections dealing with contact and stomach insecticides, we consider that it is desirable, in view of the recent development of insecticides like D.D.T. possessing both contact and stomach poisoning properties, to depart from this conventional division. We felt that consideration of the destruction of insects by toxic gases or vapours (fumigation) provided an introduction to this subject for the general reader. The chapters IV to IX deal with the older insecticides whose properties and insecticidal powers are well known. In this way it was possible to attempt to provide a clearer picture of the impact on pest control of the newer synthetic insecticides and to draw attention to the gaps in knowledge which are inherent in the "newness" of these compounds. It was not practicable to divide the book into sections devoted to the control of pests in the household, agricultural and veterinary fields owing to the overlapping involved. The discovery of the insecticidal properties of D.D.T. which are exerted over such a wide variety of insects has corrected any tendency which may have been developing among workers to think of these applications in separate compartments of the mind.

It is reputed that an Arab proverb, on translation, says something to the effect that a man remains master of the unspoken word, but becomes the slave of those he has been unwise enough to utter. In saying something about trends and possible developments we realize only too well that we become coated in the second half of this proverb. However, we were forced to realize as the book took shape that we could not evade this indiscretion. The inadequacy of much of the routine spray equipment in dispersing mists to control flying insects such as mosquitoes was emphasized during the war. Whilst being compact, the aerosol bomb remains somewhat expensive for general use and the recent American work on pocket sprayers indicates that considerable development can be expected in methods of dispersing insecticides. Provided no health hazard is shown to be involved, it is to be expected that considerable use will be made of smokes. For instance, it has



recently been shown<sup>3</sup> that the burning of cord impregnated with D.D.T. produces a smoke which is lethal to insects. Owing to the dramatic residual action of D.D.T. considerable success has been obtained with cardboard treated with D.D.T. to act as a flypaper. Recently, it has been shown<sup>4</sup> that a long-term treatment for houseflies involves the deposition of a D.D.T. film on spots which flies frequent. In this field the formulation of products possessing special fixative or other properties permits broad scope for the imaginative worker.

The importance of the physical state of the insecticide as presented to the insect is now generally recognized. D.D.T. in coumarone resin, when dissolved in a suitable solvent, provides surfaces in which D.D.T. is presented in fine needle-shaped crystals.<sup>5</sup> Parkin and Green<sup>6</sup> found that the highest toxicity against houseflies was obtained from a given amount of D.D.T. when the solution applied was of high concentration and found on microscopic examination that surfaces treated with such concentrations of solutions were covered with minute crystals of the insecticide. In tests against bed-bugs, Barnes<sup>7</sup> found that minute particles of D.D.T. produced the best results—large crystals were not so effective—and suggested that solvents which on evaporation deposits D.D.T. in the form of very small crystals should prove more economical. It is clear that these pioneer results are capable of considerable development.

For some years, insecticides have been applied over wide areas from aeroplanes and great advances have been made in the equipment and methods employed.<sup>8</sup> Already formulations of D.D.T. have been used at such a concentration that the limiting factor in the area treated in one flight is no longer dependent upon the load of insecticide which it is possible to carry but the limitation is pilot fatigue. Recently experiments have been carried out in the dispersal of insecticides discharged from air-bursting missiles.<sup>9</sup> It is certainly reasonable to expect development of such ideas for the bringing of malarious areas under control. Experiments in spraying vegetation against tsetse fly showed that a considerable portion of insecticides like D.D.T. and "Gammexane" were absorbed by the vegetation. Working on citrus in California, Ebeling<sup>10</sup> found that the addition of aluminium stearate to kerosene solutions inhibited the absorption and here again advances can be expected.





**Fig. 2.**—An early experiment in aerial spraying from a Sikorsky R.4 helicopter.  
*Photograph by courtesy of Pest Control Ltd.*

In the early days of D.D.T. considerable fears were experienced as to the possible effects of the wide-scale use of D.D.T. in agriculture in affecting the balance between beneficial and harmful insects and the effect upon fish and wild life. It appears true to say that the effect is less disastrous than was envisaged by some prophets. The use of D.D.T. in orchards does appear to lead to an increase in the population of red spider and woolly aphis. Research is proceeding in various parts of the world to discover compounds active against these pests. In fact, the suggestion of mixing D.D.T. with hexaethyl tetraphosphate (which



appears to be effective against red spider) has already been mooted. In this connection, interest has recently revived in the use of azobenzene against red spider.<sup>11</sup>

Another method of approach lies in accurate assessment of the minimum dosage necessary in practice to control a given pest and it has been found<sup>12</sup> that aerial spraying at less than one-fifth of a lb. per acre minimizes the effect on fish and wild life. The foregoing illustrates some of the problems and above all the stimulus provided by the discovery of the remarkable properties of D.D.T.

In considering the mode of action of D.D.T., Martin and Wain<sup>13</sup> produced evidence to support their suggestion that the insecticidal properties of D.D.T. are associated with the property of the compound in losing hydrogen chloride to produce the substantially non-insecticidal dichloroethylene compound. This theory was utilized by workers in the United States to produce another insecticide of this class which appears to have extraordinary properties (see Chlordane, page 178). This illustrates the amazingly rapid progress which is now being made in this field and coupled with discoveries such as the importance of the spatial configuration of the atoms in the benzene hexachloride isomers there are clearly vast possibilities for further advances.

The ingenuity of the organic chemist in the insecticidal field is illustrated by the development in Germany during the war of hexaethyl tetraphosphate ("Bladan").

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## CHAPTER II

### THE INSECT

IN attempting the solution of any particular problem of pest control, there are two major aspects to be considered; these are, firstly, the investigation into the life-history and habits of the pest and then, secondly, the selection and trial of methods and materials of control which seem most appropriate. It is unfortunately not within the scope of this book to describe the fascinating details covering the biology of world pests which have been recorded adequately elsewhere in many books on economic entomology. However, inasmuch as it is quite impossible to evolve a successful method of control for any particular pest without the closest study of its life-history, habits and environment, it is desirable that we should take a brief glance at some of the salient points concerning the insects themselves, and to note some of the problems which confront the entomologist before he can successfully prescribe control methods.

Insects belong to that phylum or tribe of animal families known as the *Arthropoda* which also includes such apparently diverse creatures as the lobster, the centipede, the scorpion, the spider and the mite. All the representatives of the *Arthropoda* are typically characterized by a bilateral symmetry in which the segmented body bears a series of paired limbs which, in many cases, have become adapted to a particular function distinct from walking, for example, to serve as antennae or jaws. A further characteristic they have in common, which distinguishes them from the majority of other animals, is the possession of a hardened covering known as *chitin* which may not only have a protective function, but also serves as an exoskeleton for the attachment of muscles. The group *Insecta* or *Hexapoda* is distinguished from other arthropods by a body divided into three distinct regions—a head bearing one pair of antennae, a thorax with three pairs of legs and usually two pairs of wings, and an abdomen devoid of legs except in a few instances. Respiration is accomplished by tracheae, a series of tubes ramifying through the body and internal organs, and opening to the external air



on either side of the insect by means of a series of holes known as spiracles.

It will be seen from this definition that entomology would appear to exclude the study of such pests as mites, which although arthropods, do not fall into the group *Insecta*, for typically they possess eight legs in the adult stage. In practice, the entomologist tackles a number of problems which lie outside the strictly academic definition, and thus economic entomology not only embraces the field of insect control, but also that of certain other crop and animal pests.

It has been estimated that insects numerically comprise 75 per cent. of all living animals of the world,<sup>1</sup> and it is therefore not surprising that they represent a real challenge to man's supremacy on the earth. They form perhaps the most remarkable group of all animals because of the extreme diversity of form and habit they have developed, covering practically the entire range of animal habitat with the exception of the deep sea. Thus, geographically, they are to be found from the Arctic to the Tropics, both in the desert and in the rain forest; they inhabit both the surface and the interior of the earth, of plants and of fresh water, while their conquest of the air is a characteristic readily apparent to the most casual observer.

The great adaptability, which must have been inherent from the ancestral primitive form, has led further and further along lines of extreme specialization, until many insects have become so closely adapted to their environment that relatively small changes in an area may lead to their virtual extinction while at the same time creating favourable conditions for other species to move in. Thus the perfect specialization, while a source of strength to insects considered as a group, nevertheless constitutes a danger to an individual species. Unlike the insects, Man, as a species, has retained his supremacy by adapting the environment to his particular needs and thus has avoided the danger inherent in extreme specialization.

The majority of insects lay eggs, although there are exceptions where living young are produced. The young insect that emerges from the egg is almost always morphologically different from its parent, and in order to reach the final state of the perfect insect, or *imago*, it must pass through changes of form known collectively as metamorphosis. In a



few families the young insect is almost an exact replica of its wingless parent, but the great majority can be divided into two classes according to the degree of metamorphosis which takes place. The first of these divisions is typified by the plant bugs and aphids in which the young are recognizably similar to their parents except that only the rudiments of wings and genitalia are present; as the young insects pass through a series of growth stages, separated by the moulting of the confining chitinous covering, the wing and genitalia rudiments progressively develop until the perfect form is attained. The immature forms of this class are called *nymphs*. The second division contains those insects in which the immature forms are markedly unlike their parents as, for instance, the caterpillar is dissimilar to the butterfly and the maggot to the housefly. In these cases there are also a series of growth stages but the great transformation of the immature form, known as a *larva*, to the perfect insect or *imago* takes place during a quiescent or *pupal* stage, a familiar example of which is the chrysalis which separates the caterpillar from the butterfly.

Nymphs are not only recognizably similar to the imago but often have similar habits so that it is not unusual to find the immature forms and the adults living side by side. Larvae, on the other hand, are often adapted to a different environment from that of the adult; thus, for instance, the larvae of the mosquito inhabit water, while the adult is free-flying, and the maggot of the sheep blow-fly lives in animal flesh while again the adult is aerial. The many variations of development may be further complicated by other factors, for example, not all insects require to mate for reproduction, or they may feed on certain plants in one season and then migrate to a different species of host for the remainder of the year. An intensive study of the life-history of a pest is therefore of primary importance in resolving the most vulnerable stages to attack.

The existence of all animals is dominated by environmental factors such as the relative abundance of water, food and shelter, and also by physical conditions such as heat, humidity and light. Mammals have obtained a small measure of independence over changes in temperature by virtue of blood-heat regulation and Man, in particular, has achieved an even greater degree of freedom by controlling his own environment



by the artificial provision of shelter, clothes, heat, water and food. Insects possess no compensating mechanism which enables them to continue their development and activity at an even rate through changes in external conditions, and fluctuations in these are reflected directly in the life history.

The presence of the requisite food is, of course, a necessity for the development of an insect and its relative abundance is one of the factors controlling the size of insect populations. The kind of food may also influence the life-history by affecting the fertility of the females or the longevity of the adults.<sup>2</sup> Many insects are able to survive cyclical periods of food shortage by the fact that a resting non-feeding stage of the life cycle coincides with these unfavourable conditions; thus many plant-eating lepidoptera in temperate zones overwinter as eggs, while similarly in more tropical zones insects may "oversummer" or aestivate during the hot dry season when the vegetation is scarce. Other insects, such as the blood-sucking bed-bug and tick, whose source of food supply is irregular, are able to survive many months without feeding and, somewhat naturally, make the very best of those opportunities which do occur.

One of the most potent factors influencing the life of insects is the temperature of their surroundings, for this not only largely controls the speed of development, but also influences the degree of activity. Many workers<sup>3</sup> have concentrated on this aspect of insect ecology, and it will be only superficially considered here. For each species there is an effective range of temperature at which development proceeds, with increasing tempo at the higher end of the scale and with a corresponding decrease at the lower end; at some point within this range is an optimum for development at which the greatest numbers of individuals develop successfully into normal adults. Immediately outside the limits of this range there are, at either end, zones at which the insect can support life for a varying period of time, and then resume development if once more brought within the effective range; outside these zones are lethal temperatures from which no recovery can take place. The lethal high temperature for the majority of insects is about  $48^{\circ}$ – $50^{\circ}$  C. and the lethal low temperature varies from a few degrees below zero to  $-14^{\circ}$  C.; the effective range is much shorter and often lies approximately



between  $10^{\circ}\text{C}$ . and  $35^{\circ}\text{C}$ . Each species has its own limits to the influencing zones and it is not therefore possible to generalize with any degree of accuracy; for this reason each species presents a fresh problem for study.

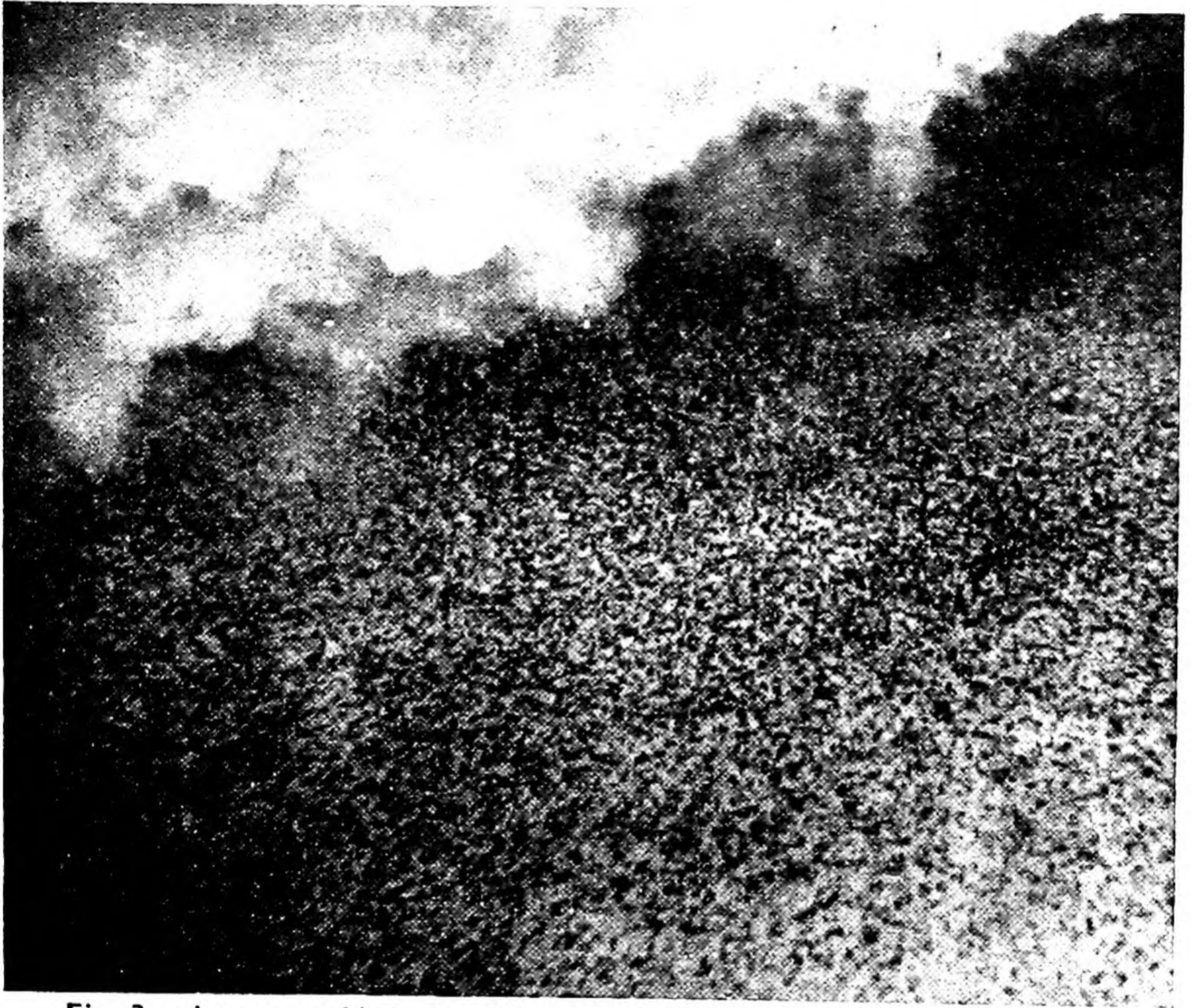
Along broad lines, the effect of temperature on insects is easily observable in the field. A species such as the codling moth develops so slowly in the temperate climate of England that only one generation is usually produced in a season; in the warmer climates of the Middle East and California, this same insect passes through five or even six generations in the season. Extremes of temperature in a season will also influence greatly the prevalence of an insect species; in temperate zones, it is generally exceptionally cold winters and springs which check the development of an insect, while in countries where hot winds occur, it is the high temperatures which may reduce the insect population.

Within the effective temperature range, there is a direct relation between the increase in the velocity of development and the rise in temperature, except at either end of the scale where small divergences occur. In nature, however, the insect is rarely subjected to an even temperature, but to variations through diurnal changes and the prevailing weather; the cumulative effect of these variations has sometimes been measured by the summation of the degrees by which the mean temperature each day of the growth period exceeds the minimum effective temperature (the threshold of development) at which development of the species under review is almost stationary. This method may serve to give an approximate estimate of the duration of various growth stages of insects, but the data used for measurement, *i.e.* the mean air temperature for twenty-four-hour periods, does not take into account the actual temperature and humidity changes of the micro-environment surrounding the insect and is, in general, too vague to permit of close correlation.

The effect of temperature on the activity of insects is not often readily apparent in temperate countries, but may be very marked in warmer climates. To a great extent the daily programme of a locust swarm is dictated by the prevailing heat; in cold night hours the locusts are incapable of movement and can be swept off the ground and bushes into sacks by the inhabitants who collect them for food; from dawn to



approximately 8.0 a.m. they can move, but with a little difficulty, and this period is spent in sunning themselves; for some two hours thereafter they will feed and then the swarm will take off in flight to redescend to the ground in the late afternoon with the lowering of temperature.



**Fig. 3.**—A swarm of locusts. *Photograph by courtesy of Plant Protection Ltd.*

This programme fluctuates with the daily variations in temperature, but the variations can themselves be predicted by closely watching the trend of the thermometer.

In a similar manner, but generally to a lesser degree, the daily temperature influences the activity of all insects and, in part, determines their habits.

The humidity of the air is also another environmental factor of some



importance to insects, but its influence is not so clearly marked as that of temperature. Although this field of investigation has not attracted many investigators, there is nevertheless a body of evidence which indicates that for each species there is an optimum humidity for development, and that either extreme conditions of moisture or dryness may prove fatal. All the factors which together make up the environment influence in some degree the development of each species of insect and, by a careful study of them, it is possible roughly to forecast the manner in which climatic differences will influence the prevalence of a pest.

An integral part of the study of a pest is the investigation into its behaviour. With the extreme specialization of form, there has been a similar development of instinct which has, in certain species, reached such a perfection in its chain of reactions that it is difficult to believe that the insect does not "think". Indeed, with certain insects, it appears that behaviour may not be entirely mechanistic, and that at least some degree of freedom of choice may be exercised.

Lloyd,<sup>4</sup> studying a parasitic insect, *Oenocyrtus kuwanae* Howard, which lays its own egg within that of the gypsy moth, found that if the parasite is presented with both healthy host eggs and those already parasitized by another individual, it is able to appreciate the difference and selects only the healthy eggs in which to oviposit; furthermore, if *Oenocyrtus* is presented only with eggs previously parasitized, she tends to restrain oviposition, but if the urge to lay is too strong, she selects those eggs containing the youngest parasite stage, thus giving her own egg the best chance of survival. This contribution to insect psychology is of such interest that part of Lloyd's conclusions are quoted here in full:

It is concluded that the oviposition response is to a perceptual complex of stimuli which is such that the female tends to choose those hosts in which its progeny are able to develop. This accords with the classical view of the instinctive nature of animal behaviour, and with the Gestalt thesis of reactions to relations in the perceptual field. These perceptual complexes take the form of complete wholes such as an unparasitized gypsy moth, a gypsy moth egg containing a parasite larva, etc., and when a female is confronted with a choice of such host types, one host is selected in contrast to another, the selection being that with the most complete set of characters of a normal unparasitized host. This apparent striving for the ideal unparasitized host seems to be a dominant factor also in the exercise of restraint when parasitized hosts only are available. It is inferred that the synthetic relating activity in such behaviour is analogous to a psychological phenomenon in man.



While it seems possible that in certain conditions, some insects may exercise a freedom of choice within narrow limits, it appears to be beyond doubt that, in general, insects should be considered as being machines whose life is guided by a series of reactions to a complex set of stimuli both external and internal. Even such apparently "intelligent" phenomena as the recognition of one ant by another is explained by the fact that all individuals inhabiting one colony have a characteristic odour; when an ant is washed and placed back in its own colony it is treated with the same hostility accorded to a stranger ant.<sup>5</sup>

The behaviour of insects to external stimuli is a field which has attracted considerable attention, and has formed the basis of a number of attempts to reduce pest infestation. These reactions, or *tropisms*, have been broadly classified according to the operating factors such as light, odour (chemical), moisture, wind direction, and they may be positive in attracting the individual to the source, or negative and repellant. Of the various tropisms only *phototropism* (reaction to light and colour) and *chemotropism* (reaction to chemical stimulus) appear to hold any real promise as phenomena which can be turned to practical use in pest control.

It has long been known that light is a prominent factor determining the behaviour of insects, some of which are attracted to it such as the proverbial moth to the candle flame, while others are negatively phototropic such as the termites which construct tunnels in which to travel, or the cockroach which slithers to shelter when the light is turned on. Even this simple division of reactions is complicated because those insects which are positively phototropic show different graduations of response to light attraction; thus butterflies are stimulated by high intensity light and fly by day while moths are attuned to low light intensity and, while ignoring daylight, are attracted to artificial illumination.

The mechanism of the attraction appears to be in the involuntary orientation of the insect towards the direction of the light rays so that every movement away from the source of light is checked, while movements towards the source are uninhibited; a moth will therefore seldom approach a candle flame in a direct line, but travels a diminishing spiral path round it until it is so close that the light stimulation permits no deviation and it enters the flame. Conversely, negatively phototropic



insects involuntarily orientate themselves away from the direction of the light rays and uninhibited movements take them away from the source of light. The phenomenon has, of course, been stated in its simplest terms for in natural conditions it is seldom or never that the insect is subjected to only one stimulus, and its ultimate behaviour will depend on a variety of operating factors; a bed-bug, for instance, normally shuns the light, but if it is very hungry it will reverse this behaviour when stimulated by the presence of a victim and attack him in daylight, though all the time taking advantage of shadow whenever that is possible.

The attraction of night-flying insects to artificial light has led to a number of attempts to utilize this reaction to trap nocturnal pests, particularly moths and beetles which attack crops. Although some results have been promising experimentally, it appears doubtful if this method is likely to succeed as an economic method of control, for in order to ensure any real diminution of population, a great number of traps must be used and even then many insects evade capture, or are trapped only after they have deposited their eggs. Light traps have, however, been the source of much data regarding nocturnal flying insects, and in this country Williams,<sup>6</sup> who devised a mechanical method of segregating the catch according to the period of the night, has published interesting information on the incidence and habits of British night-flying insects in correlation with the season of the year, the time of night, and the prevailing weather.

It has now been established by a number of workers that insects are able to differentiate between certain colours, but their range of perception differs from that of humans. Von Frisch<sup>7</sup> in his classical work with the honey bee showed that this insect can be trained to associate sugar solution with blue, yellow and black, and will continue to visit these colours even after the food has been removed; it cannot, however, distinguish between black and red, or between various shades of blue or yellow; on the other hand, it has been shown that it perceives ultra-violet as a colour. Similar observations have been recorded on other insects and it thus appears that the visual range of perception, as compared with that of humans, is displaced towards the violet end of the spectrum. Little use has been made of the attraction or repulsion of



insects to various colours as a means of pest control although Imms<sup>5</sup> has suggested that the effect of light traps rich in ultra-violet light might be worthy of more thorough investigation.

Chemotropism, the reaction to chemical stimuli, plays an important role in insect behaviour. In nature, stimuli of this type may be classified as odours or tastes, depending on whether they act at a distance or in contact with the insect, but it is not certain whether there is, in fact, any clear delineation between the two. In any case, there are marked differences between the mode of perception and that of humans for the receptor organs are believed to be located on the antennae, the feet, and other parts of the insect body and are not concentrated in the oral region; an insect does not therefore need to take a mouthful of a substance to ascertain the attractiveness or otherwise of a material and this may have an important bearing on the use of stomach poisons.

Odours appear to aid many insects in the location of food, their mates, or the most suitable place in which to deposit their progeny. Conversely, there are odours which are disagreeable and repellant and in nature these are utilized by certain species who are able to emit offensive secretions which render them unpalatable to their enemies. It has been possible in the laboratory to isolate a number of chemicals to which insects show a greater or lesser degree of attraction and repulsion; these are sometimes the same or akin to those which the insect is likely to meet in its normal life, for example, the lower alcohols and their esters which are attractive to some insects feeding on over-ripe fruit, or ammonia which attracts flies habitually laying their eggs in decaying manure. In other cases, insects show a definite reaction to chemicals they are never likely to meet except in the laboratory. Both odours and tastes which insects find attractive or repellent may cause the reverse reactions in Man or may not even be perceived by him at all.

The idea of using a chemical attractant to entrap insects or to tempt them to swallow a lethal dose of poison is not new; lepidopterists have used sugar or treacle smears on trees to attract night-flying insects, and sugar and beer have been incorporated in many household recipes to deal with ants and cockroaches. It is only comparatively recently that this idea has been extended to wide-scale operations aimed at securing control over economic crop pests. Many attempts have been made to



utilize the attractive quality of chemicals and natural materials in traps, but although there have been partial successes in field trials and proprietary products sold, the method has never been adopted on a large scale for, as with light traps, an enormous number of insects must be caught before the total population is materially reduced; chemical traps have been found useful to estimate the appropriate time for more conventional control measures to be applied, as they form useful indicators of rises in pest numbers.

The use of materials to make poisons more attractive to insects has been a much more rewarding field and holds promise of future development. Sugar and molasses have so far been the products most commonly used, often without sufficient justification, for although many insects possess a sweet tooth, there are others for which these mixtures hold no attraction. During the last twenty years, the control of locusts has made great strides by utilizing poison bait against the young locusts or hoppers; for some time it was believed that the incorporation of molasses in the bait, whose other ingredients were bran and sodium arsenite, was a necessity as an attractant,<sup>8</sup> but it is now fairly generally agreed that the sweet substance holds no attraction and, in fact, may even be slightly repellent to locusts; the true attractive power in the mixture appears to lie in its bran and moisture content.<sup>9</sup> There is no universal attractant and if this method is to be developed fully it seems obvious that it will be necessary to investigate the reactions of each pest to chemical stimuli and then to choose the materials which hold the most promise.

An obvious field which would well repay continued investigation is the use of baits to control those insects whose larvae are destructive of crops, but whose adults only visit the host plant to lay their eggs and not to feed. A case in point is that of the fruit-flies, serious pests in sub-tropical areas; the adult fly only visits the tree in order to lay its egg within the fruit where the maggots hatch and feed within the protection of the fruit itself. A considerable degree of control has been obtained over the Mediterranean fruit-fly in Palestine by spraying the fruit tree with coarse drops of a poison suspension incorporating sugar; although the adult flies do not normally find food on these trees, they are attracted to the sweet drops on the foliage and imbibe enough to kill them.



Although poison baits have proved of immense value against such insect pests as cutworms, armyworms, mole crickets and locusts, the route by which they have been discovered has been largely fortuitous and empirical. The reverse may be said of repellents which have received intensive investigation. The need for repellents to ward off hungry mosquitoes and sandflies has been felt by everyone who has lived in infested areas; palliatives have long been used, ranging from citronella oil to the wood creosote used by the Lapps, which is surely more painful than any insect bite. In the late war, the necessity of protecting troops against malaria-bearing mosquitoes stimulated research in this problem and at least three chemicals are now known which will repel mosquitoes for a number of hours while at the same time they are not disagreeable to man. Repellents have not yet been used with any real success for the protection of crops against insect attack, although the possibility of development in this direction cannot be ruled out.

In natural conditions, an insect is never subjected to only one stimulus at a time, but to many, and the response to the combined exciting factors is a co-ordinated reflex behaviour somewhat loosely defined as instinct. In other words, individuals of the same species subjected to the same combined stimuli behave automatically in the same manner, although relatively minor modifications may occur. It must, however, be carefully noted that the internal stimuli are as important as the external; the presence of a suitable host will not arouse the interest of a parasitic wasp until she is physically ready to lay her eggs, nor will external conditions make a caterpillar spin its cocoon until it is fully fed.

As Lefroy<sup>10</sup> has pointed out, the variation in instinct between two members of the same species is so small that it is possible to regard insect species as not only definable by morphological characters, but also by behaviour, and on this reasoning every species can be treated as an individual; when the life-history and habits of a particular insect have been discovered, it can safely be predicted that in the same circumstances, all the insects of that species will have the same life-history and that with a given departure from normal circumstances, all will behave alike. There are minor variations from this rule, as, for instance, an



insect species may have different host plants in different countries, but in the main it holds true and is one of the keystones on which the entomologist builds his research and plans.

In this chapter, no attempt has been made to cover in detail the biology of insects. It is hoped, however, that sufficient has been said to emphasize the diversity of development and reactions to be found within this large and important group of animals and to show that only broad generalizations can be made. Each species of insect presents a fresh problem for study and the successful application of control methods depends on the intimate knowledge of the life-history and behaviour of the pest and the niche it fills in its natural environment.

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## CHAPTER III

### OUTLINE OF PEST CONTROL

SINCE the time when primitive man first scratched the soil in an endeavour to secure a certain supply of plant food rather than to be dependent on the vagaries of wild vegetation, he has had to contend with a host of factors inimical to domestic cultivation; one of the most potent of these factors is the competition suffered from insects. The great strength of the insect family, considered as a whole, lies in its adaptability, for it has representatives in almost every conceivable environment—the air, the soil, fresh and brackish water, both on the surface and within plants and animals and even in pools of crude petroleum oil;<sup>1</sup> it is,

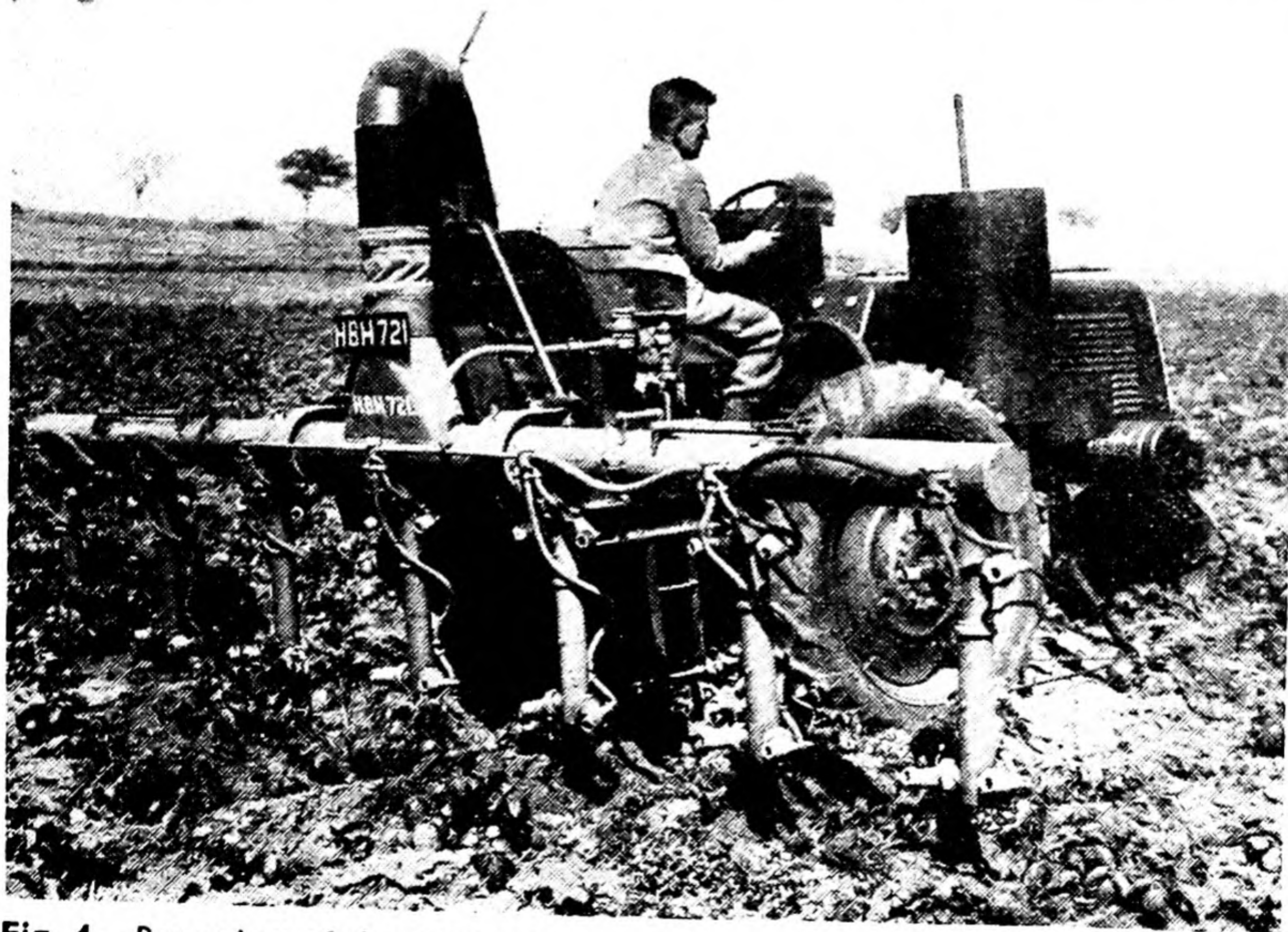


Fig. 4.—Rear view of the Agro spraying machine. Photograph by courtesy of Plant Protection Ltd.



then, not surprising that there is no plant or animal which is not subject to attack in a greater or lesser degree.

In his efforts to provide the most favourable conditions for his crop and thereby creating an artificial environment, man automatically provides conditions which will be favourable to some insect pest, either by disturbing the natural balance which would otherwise control it or even more simply by providing it with extensive areas of a suitable host plant on which it can feed and reproduce. The situation has been further complicated by the fact that many varieties of domestic plants have been bred for the qualities most immediately desirable to man, as for example, high yield, taste and colour, and that in the artificial selection which has taken place, many of the characters which convey a certain resistance to attack in the naturally occurring wild plant have been eliminated.

Methods for overcoming some of the obstacles to plant cultivation were recognized at an early age; thus it has long been known that the fertility of the soil can be restored by the application of dung, and that erosion may be checked by terracing. Insect control, however, has been hampered by lack of knowledge which has attributed attacks to wrathful gods and origins beyond human control and it is only in the last century that science has advanced sufficiently, first to appreciate the problems in their true light, and then to provide the materials and methods for solving them. The losses to national economies resulting from insect damage are enormous and rarely comprehended; thus Neave<sup>2</sup>, in an attempt to bring home the magnitude, computes on a conservative basis of a 10 per cent. loss in total crop yield due to depredations by insects, that not less than one-tenth of the human effort in the British Empire on basic industries such as agriculture is dissipated by our insect enemies.

To the individual farmer, successful pest control may often represent the margin between ruin and prosperity and suitable methods whereby insect damage may be kept within economic bounds have become a necessity in the present world with its demands for increased food production. The problem of pest control may be approached in a number of ways of which the most important are cultural practices, biological methods and the application of chemical insecticides.



**Cultural practices in pest control**

There are certain cultural practices, using the term in its broadest sense, which aid the farmer in his fight against insect pests. Some of these are primarily for other purposes but also have a significance in the reduction of pests as, for example, ploughing which may destroy the habitat of a soil insect and expose it to desiccation and to the action of natural enemies; a further illustration is afforded by the practice of crop rotation, which although designed primarily for the conservation of soil fertility nevertheless is a potent factor in reducing pests by withholding the necessary host plant and so starving them out. Other operations have for their sole aim the discouragement of pests, and amongst them may be numbered alterations in the date of sowing or planting out, either to avoid periods of high pest incidence or to ensure plants well advanced in growth when they are not so vulnerable to attack and also farm and orchard sanitation in which trash and prunings which harbour pests are destroyed by fire.

Within the general scope of this section lies also the practice of using varieties and strains which are more or less resistant to pest attack; thus the problem of phylloxera on grape vines has been largely solved by the use of resistant American stocks, while considerable attention has also been paid to the possibility of finding strains of sugar cane resistant to froghopper attack. The development of this line of protection is necessarily slow and entails much lengthy research, and pending the solution of each particular problem other methods of pest control must be used if they are available. The general health of the plant has also much to do with the incidence of attack and in some cases the suitable selection of fertilizers may confer considerable protection; thus Andrews<sup>3</sup> showed that the infestation of tea bushes by *Heliopeltis theirora* could be greatly minimized by using fertilizers which made available a high ratio of potash to available phosphate in the soil; it is generally known that weakened trees are more subject to attack from scolytids and other boring beetles. While unfortunately the majority of pests are not deterred from attacking plants in perfect health, and even enjoy the extra succulence provided, there is an interesting field in the investigation of the relationship between plant nutrients and insect damage.



### The biological control of insect pests

All insects are subject to biological control which is the natural restraint placed on their increase in population by biotic factors such as parasites and predators. The use of biological control as a measure against insect pests therefore consists of an endeavour to sway the balance between a pest and its natural enemies in a direction favourable to man;<sup>4</sup> this may be accomplished either by measures calculated to favour the parasites and predators already in the locality or, more usually, by the introduction of an additional species of enemy.

The organisms which may be used to obtain biological control fall into three classes: 1. Bacterial, "polyhedral" and fungal diseases; 2. Vertebrate predators; and 3. Invertebrate predators and parasites. The organisms responsible for insect diseases, while common in the field and occurring sporadically as devastating controls have so far proved unreliable and generally useless when artificially introduced. Many students<sup>5</sup> have endeavoured to make practical use of the lethal character of this group but the majority have given their considered opinion that such factors are ungovernable by man and are therefore unsuitable themselves as controlling agents. A notable exception to this group of workers is Metalnikov<sup>6</sup> who claims at least temporary successes following the application of pathogenic spores. Experiments utilizing the fungi have not been so extensive but those, for instance, with *Empusa musci* and *Empusa grylli* have not given encouraging results. It seems probable that, while in nature disease may be the direct agent controlling the insect, there is a more potent factor, such as humidity, controlling the disease itself and successful introduction of pathogenic organisms can only be made when all the environmental factors are suitable.

There is no doubt that vertebrate predators, of which the most important are birds and rodents, destroy large numbers of noxious insects but the value of this control is not agreed. As Thompson<sup>7</sup> has pointed out, the population of such predators is probably entirely independent of one particular species of insect and while they may consume an average quantity of insects each year, this will not be related to the abundance of any particular pest. On the other hand, Hardy<sup>8</sup> believes that in many cases of epidemic infestation vertebrate predators exert a greater



control than is usually credited by the majority of authorities. However important a place vertebrate predators may fill in naturally occurring biological control they are, in general, unsuitable subjects for introduction as their extreme lack of specificity may lead to unforeseen and dangerous disturbances in the biotic environment of the whole area. It therefore appears that while the value of some of these predators is considerable, and those already established should be protected and encouraged, fresh introductions of new species should only be made after careful investigation into the niche they would occupy in the general plant and animal complex.

Although the category of invertebrate predators and parasites includes representatives from many phyla, the chief enemies of insect pests are undoubtedly those of the same class, *i.e.* other insects, probably because their numbers and reproduction rate are of the same order as that of the pest itself. A further advantage in the employment of this class of enemies is their extreme specificity for a parasite, if properly selected, is unlikely to change its habits and forsake the noxious host for a beneficial one. Two methods may be used for the employment of insects in biological control; the first is the artificial increase of insect enemies already established and the second is the introduction of new species into the complex.

The intensification of the action of natural enemies presents the disadvantage that, as it is accomplished by artificial adjustment of the naturally occurring complex, the measures by which it is executed must be practised each year. Practical success has been claimed for methods of conserving parasites of pests where ordinary agriculture procedure results in their destruction; thus Decaux<sup>9</sup> claimed economic control over apple-blossom weevil (*Anthonomus pomorum*) by preserving the infested buds in cages until after the emergence of parasites which were then released in the field; the normal practice is to burn the infested buds thus destroying the beneficial parasites. A further striking example is cited by Holloway *et al.*<sup>10</sup> who pointed out that the burning of stubble after cutting sugar cane is not an effective method of decreasing the population of the sugar-cane moth borer (*Diatraea saccharalis*) as this practice destroyed many of the insect enemies which would normally hibernate in the debris; a practical trial over a period of seven years



demonstrated the validity of their arguments by substantially decreasing borer infestation when stubble was left unburnt. As the control of a pest by natural enemies is dependent on the ratio of the populations it follows that an artificial increase in the numbers of enemies will alter the balance in their favour; following this principle, endeavours have been made to effect this intensification by the artificial breeding and hibernation of parasites and predators. This method needs careful investigation in each particular case before the probabilities of success can be estimated, for although a pest population may have a relatively low percentage parasitism, the actual number of parasites in the field may be extremely large, and the number which must be added artificially to cause any appreciable increase may be well outside the bounds of economic possibility. The number of cases in which this method has been applied are limited but for some years *Trichogramma* has been artificially reared and released in the West Indies in order to aid the existing population in controlling *Diatraea saccharalis* and in California the coccinellid *Hippodamia convergens* has been collected in autumn for storage in refrigerators until spring when it is liberated to control infestations of aphids on crops. In both these cases there is considerable doubt as to the value of such artificial increases in population and this particular field of biological control is generally regarded as being unprofitable if other methods are available.

By far the greatest use of biological control has been made by the introduction of new species of insect enemies and this method is particularly favourable where the insect pest is itself an accidental introduction into a new area where the native parasites are often unable to adapt themselves sufficiently well to exert any considerable degree of control. Hardy<sup>11</sup> has reviewed the complex factors concerned in the selection of a suitable insect enemy for introduction; the introduced parasite or predator should not only be able to survive in the new climatic environment but must also adapt itself advantageously to the stages in the host life-history, *i.e.* there must always be a supply of the correct host-stage at the appropriate time; furthermore, as the time taken for a parasite to reduce an insect infestation depends on the relative reproductive rates of host and parasite, the introduced insect enemy should be one capable of developing a high potential reproductive rate



in the new environment. Other factors such as the avoidance of multi- and superparasitism must also be taken into account before a new introduction is made.

The rapid development of the biological method of control in recent years has led to the trial of so many experiments that it would be out of place to try to present a compilation of them, especially as these have been competently reviewed by Sweetman.<sup>12</sup> It should be emphasized, however, that because the relation of the insect pest to its enemies is always in the nature of a balance, whether it be favourable to the one or the other, there can be no question of complete elimination of pests by this method. Furthermore, the introduction of a new enemy is a slow and laborious process and the factors so complex that the chances of success are small, although the rewards are great. Biological control is thus peculiarly suited to problems such as the control of forest insect pests where often the vast extent of the area subject to damage permits of no mechanical or chemical methods for economic reasons. For the great majority of insect pests, control by chemical insecticides remains the method which will give the surest and most predictable results.

### Chemical control of insect pests

Although in ancient times various recipes, some of which were simple but others plainly obnoxious, were recommended for the control of insects infesting plants, it is very doubtful if any of them accomplished more than a symbolic cleansing. The real history of chemical control began in the middle nineteenth century when anxious farmers in the United States were faced with the invasion of the Colorado beetle (*Leptinotarsa decemlineata*) into cultivated potato lands and took the unprecedented step of applying arsenical poisons onto crops which were destined for human consumption; the arsenicals proved effective as a beetle control while the prophesied human mortality did not occur, and from that time onwards the development of control by insecticides has made steady progress. With the realization that insect attack could be suppressed, at least below the level of economic importance, came the need for the close study of the living insect in the field and today applied entomology is a science in which the entomologist and the chemist bear equal responsibility.



The suitability of a chemical to be used for insect control is not merely its degree of toxicity for there are a host of other factors to be considered; chief among these are the action on the plant and the cost of the product, while a secondary but vitally important consideration is the ease of application.

Before any detailed survey of the insecticidal field can be made, it is necessary first to give brief consideration to the broad classification of insect pests and the types of insecticides which can be most usefully applied for their control. The insects may be mostly conveniently divided into classes by their habits, as:

1. The chewing insects which bite into the plant surface and ingest the solid tissues. Representatives of this class are the caterpillars and leaf-eating beetles and the damage they cause is readily apparent to the naked eye. The usual method of controlling this class of pest has been by means of a protective insecticide which covers the plant surface with a deposit of poison and is ingested with the food.

2. Suctorial insects which have mouth parts modified into piercing and sucking organs and which feed on the plant juices but do not ingest solid food. Aphids, plant bugs and scale insects are examples of this class and the damage they cause is not so readily apparent but is more insidious in its effects. A protective layer of poison for ingestion into the stomach is useless against suctorial insects which are taking their food from the plant interior below the surface. It is therefore necessary to use a direct poison which will kill the pest by simple contact with some part of its exterior.

The division of insecticides into "protectives" and "contacts", while forming a convenient classification for the purpose of discussion, is nevertheless wholly artificial as a number of chemicals will act in either capacity; it has been made even more meaningless by the recent development of the residual contact insecticides, for whereas the old contact insecticides were so ephemeral in their action that it was necessary to hit each individual insect at the time of application, this new class can be truly protective and applied to the plant surface some time before the expected incidence of the pest.

The older type of protective chemicals act purely as stomach poisons





**Fig. 5.**—Damage to Hazel by winter moths. *A Shell Photograph.*

and the majority of them are relatively simple inorganic metallic salts. As both insects and plants are composed of the same fundamental protoplasm, it is scarcely surprising that agents toxic to the one are also likely to damage the other, and one of the prime considerations in the selection of a chemical controller is its degree of phytotoxicity; with stomach poisons the problem of ensuring differential action to insect and plant is overcome by the use of insecticides which, by reason of their insolubility in water, are harmless alike to plant and pest unless ingested by the latter when chemical reactions in the stomach set free lethal soluble compounds which are absorbed by the gut wall. The relative degree of "safety" as regards the plant tissue is well illustrated by the arsenical compounds, for whereas the soluble sodium arsenite, although



a powerful insecticide, cannot be applied to plants because of extensive foliage burning, it is possible to use the almost completely insoluble lead arsenate without incurring plant damage; similarly it is the practice in Palestine to use sodium fluosilicate for the control of the grape berry moth (*Polychrosis botrana*) on grape vines in the more arid, dewless areas but in regions of nightly dew this chemical causes extensive burning and the less soluble but more expensive barium fluosilicate must be substituted.

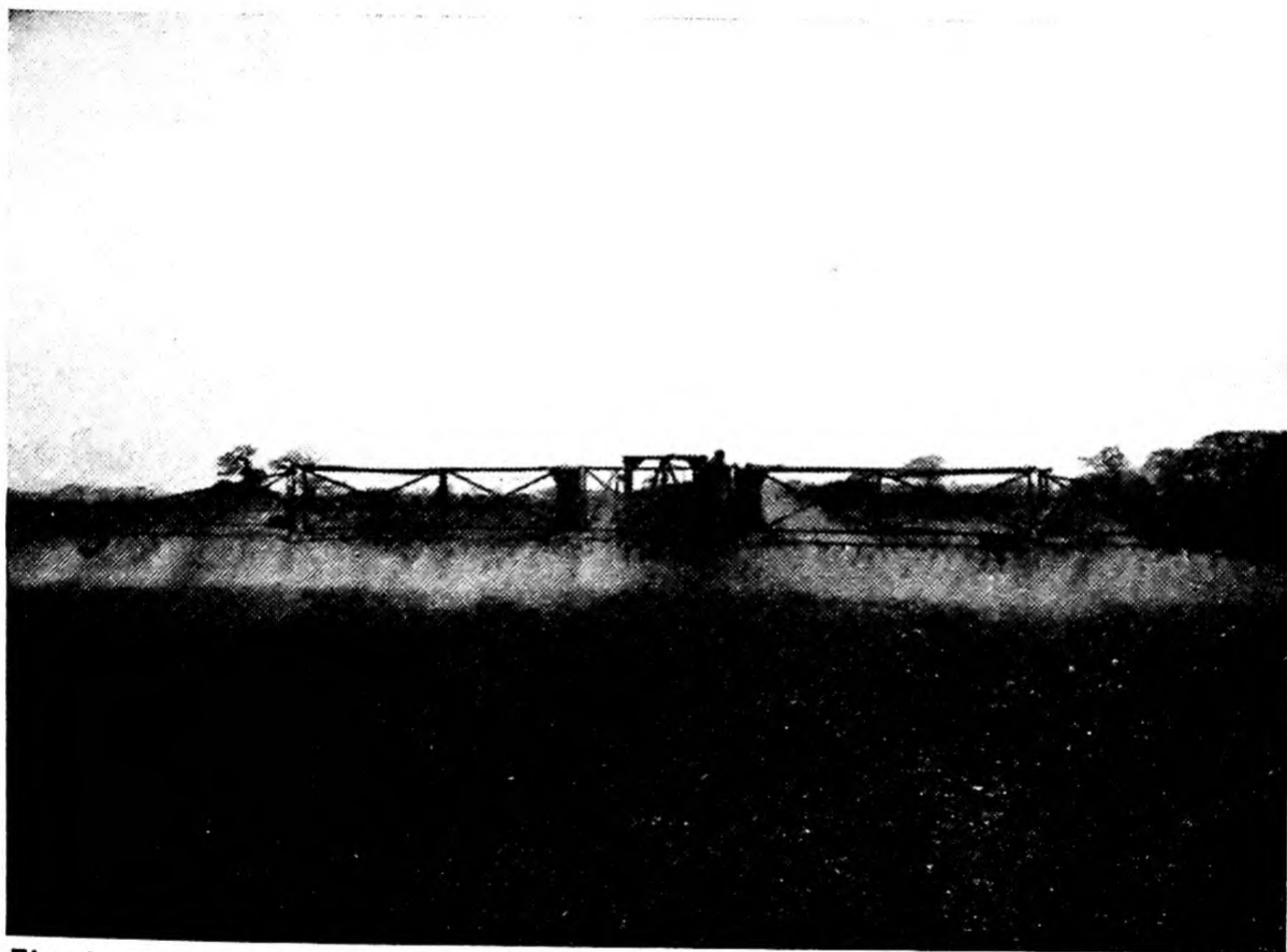
The relative toxicity of stomach poisons to insects appears to be closely related to their instability, for unless their decomposition into lethal soluble compounds takes place with some rapidity in the insect intestine, they may pass out of the body unchanged as excreta. Furthermore, the toxicity of any one chemical may vary with different species of insects. A possible explanation of both these phenomena has been offered by Swingle<sup>13</sup> who examined the *pH* range of the digestive secretions in the intestine and correlated this with the relative amounts of soluble arsenic set free from various arsenical salts; thus, with insects having mid-gut digestive fluids with a *pH* value less than 6, magnesium arsenate is more soluble and more toxic than lead arsenate ( $\text{PbHA}_5\text{O}_4$ ) while exactly the reverse holds true for insects whose digestive secretions are alkaline.

The relative speed of the reaction in the insect stomach may have considerable bearing on the efficiency of the stomach poison for there is evidence that some insecticides are distasteful and irritant and the insect may regurgitate the poisoned food or abstain from eating before a lethal dose has been taken. Furthermore, even if the chemical is palatable, unless the poison is reasonably quick in its action, the insect may cause considerable damage before it finally succumbs. The ideal stomach insecticide is therefore one which strikes a careful balance between the one extreme of being so unstable that soluble phytotoxic compounds are formed on the plant and the other extreme of being too stable to be readily lethal to the pest.

The specification for a stomach poison when there is no need to consider phytotoxic effect is by no means so stringent, as it is only necessary to consider the toxic effect to the pest, the cost and availability of the material and the ease of application. Such instances arise in the use of



poisoned baits for the control of pests such as locusts and cutworms; here the most commonly used chemical has been sodium arsenite mixed with bran or some other suitable carrier which can be moistened. It is probable that in the near future the compound will be replaced by benzene hexachloride, which not only gives a quicker kill and is relatively safer to mammals, but is also psychologically more satisfying to the farmer for he can see his enemies dying in the open, whereas with sodium



**Fig. 6.**—Spraying for the control of weeds in corn. *Photograph by courtesy of Pest Control Ltd.*

arsenite the sick insects hide away in holes and crevices to die and the infestation apparently just fades away.

In the application of a protective stomach poison, it is the aim to secure an even deposit over the whole of the exposed plant surface; this is desirable to ensure that any pest will ingest poison as quickly as possible in whatever part of the plant it may be situated and is of especial



importance with such insects as the codling moth (*Cydia pomonella*) which are only surface feeders for a period of hours, after which they bore into the interior and are thus protected from external action. To ensure permanent protection during pest incidence, it is necessary to renew the deposit of insecticide from time to time as it gradually becomes "weathered off" by the action of wind and rain, and moreover, in the case of growing fruits with rapidly expanding surface areas, the deposit would become too thinly spread if it were not renewed; thus the number of applications of an insecticide for the control of a particular pest will be dependent on the period of pest incidence and the rate of weathering, and will vary in different localities according to these factors. The time of application is not so critical as long as the poison is applied before the pest appears and is renewed before the old deposit has weathered away.

The direct insecticides are those which kill by intimate contact with the pest and, within the broad definition, this includes not only those which apparently act by direct penetration of the body wall, but also the fumigants which gain entry *via* the tracheae and the oils which may kill either by direct penetration or with a simple mechanical action by so coating immobile stages of the insect that they are stifled.

Many of the contact insecticides are organic chemicals extracted from plants; examples of these are rotenone, pyrethrum and nicotine. The mode of action of this class varies with each agent, for whereas Hartzell<sup>3</sup> considers that death following treatment by pyrethrum is due to the destruction of the central nervous system, the lethal properties of rotenone would appear to be connected with interference to the respiratory system; most of them are rather specific in their action and there are marked differences in their speed of action and in percentage recovery which may take place. Many of them are ephemeral in their action, for they can lose their lethal properties quickly after treatment in the field, and thus the timing of the application is of great importance when they are used as pest controls; on the other hand this rapid decomposition can be a material advantage as they may be applied to plants close to harvesting time when other classes of insecticides would leave undesirable poisonous residues dangerous to humans and animals.



The discovery of the new residual contact insecticides, such as D.D.T. and benzene hexachloride, is likely to bring about a fundamental change in control methods as applied to certain pests, for they combine some of the advantages of both protective stomach poisons and the older contact insecticides. In the first place, the time of application is not so critical, for their persistent lethal properties not only enable the farmer to apply them well before the expected incidence of the pest, but their extended action may enable one application to take the place of two treatments which were previously necessary; secondly, it is not so important to ensure a complete coverage when they are directed against mobile stages of insects for even if an individual pest escapes contact at the time of spraying or dusting, it is likely, sooner or later, to traverse part of the surface on which a poisonous deposit has been laid. Sufficient experience, however, has already accumulated to show that although the residual contact insecticides mark a great advance in pest control, they are not the universal panacea for all pest troubles, and have their own particular disadvantages; it can therefore be confidently anticipated that all the classes of insecticides will continue in practical use for some considerable time to come. In certain fields it has become the practice to combine insecticides, either to secure control over a range of pests or to secure a stronger or quicker toxic action; thus an oil spray, which is itself toxic to red spider, may be combined with D.D.T. whose primary purpose is to kill other species of pest and a further example is seen in the composition of the majority of flysprays which contain a "knockdown" agent, such as pyrethrum, and D.D.T. as the slower acting but more lethal component.

### **The application of insecticides**

Few insecticides are suitable for use in the undiluted form and it is usual to control the dosage and to secure even distribution by mixing the active agent with a neutral "carrier"; the carrier may be an inert dust when the material can be used in powder form, or it may be a liquid in which the insecticide is dissolved, suspended or emulsified. The most usual carrier for sprays is water which is generally available and cheap; the majority of the protective stomach poisons are insoluble in water, and therefore are applied as suspensions, due regard being paid to



particle size and agitation in the spray tank to ensure an even distribution of the active material throughout the liquid. Those liquid insecticides which will not mix with water, of which petroleum oil is a notable example, are made up into an emulsion so formulated that it remains stable in the spray tank, but on impact with the plant surface separates into the two component phases, leaving the active material as a continuous film over the plant surface while the water runs off onto the ground or else evaporates. More complex systems are also used in spray treatments, for water may be used as a carrier, by means of an emulsion, to secure an even film of petroleum oil which is itself acting as a carrier for an ingredient soluble in the oil but not in water. The main disadvantage of sprays in general use to-day is the relatively enormous quantity of water employed, the handling of which represents a high proportion of the total labour costs of treatment.

With dusts, on the other hand, there are none of the difficulties associated with the handling of liquids and they do not need such complicated machines for their dispersal. The costs associated with the handling of large volumes of water are eliminated and insecticides in this form are particularly suitable for applications where no suitable source of water is available or in certain operations such as aeroplane work where the payload of the machine limits the weight that can be carried. It is generally considered, however, that an insecticidal dust is not retained with the same persistence on plant surfaces as deposits applied by means of spray; moreover, it is not possible to provide a full range of plant protectives which can be used as dusts, for example, there is no equivalent of petroleum oils.

The trend in modern developments of applicational methods is dominated by the increasing cost of labour and the majority of experiments are devoted to increased mechanization by which manpower can be reduced to the minimum and to the elimination of the bulky inert carriers which entail high handling costs. One obvious line of attack has been the development of large semi-automatic machines which can operate at speed by use of the conventional formulations of plant protectives. A more progressive direction is the use of concentrated insecticides without the incorporation of a large bulk of water acting as a carrier; three methods have been evolved to accomplish this end, the



first involving the use of a blast of air for the dispersion of the concentrate, the second involving the use of a fog produced by the heat volatilization of a toxicant dissolved in a suitable petroleum oil and the third entails the use of a toxicant aerosol released from a "bomb" by means of a propellant gas. The principles of these new methods are not new, but it is only recently that the chemist has been able to provide suitable toxicants and carrier solvents to enable the knowledge to be applied successfully in the field; each of the methods now being tried has its own particular advantages and disadvantages and it is as yet too early to predict which of them is likely to become the successor of the practices in general use to-day.

### Spray supplements or adjuvants

In the formulation of insecticides for use in the field, it is often necessary or desirable to add ingredients which, although they add nothing to the direct toxicity, nevertheless form an integral part of the preparation. For instance, oils which play such a prominent part as plant protectives are immiscible with water and thus require an emulsifier to effect adequate dispersion in the oil-water spray, and similarly, it is desirable to incorporate a wetting and suspending agent in a powdered concentrate which is to be applied as a water suspension. These supplementary agents fall broadly into four classes: emulsifiers, wetting and spreading agents, stickers and dispersing agents.

Some of the earliest emulsifiers to be used were soaps, but although these possess some very desirable characteristics, they suffer from the great disadvantage of forming insoluble compounds of calcium and magnesium when mixed with hard water, and also of being incompatible with many of the important plant protectives such as lime sulphur and Bordeaux mixture. For this reason, attention was turned to formulations incorporating the more recently discovered synthetic surface-active agents which include cationic, anionic and non-ionic\* types; these have been surveyed by Martin<sup>3</sup> and others, but there is still an important field into the research of the most suitable of these chemicals for emulsification of the various types of spray emulsions. Certain non-synthetics

\* Ions, atoms, or groups of atoms, which have gained or lost electrons and therefore carry an electrical charge. Cations, positively charged ions. Anions, negatively charged ions. Non-ionic, carrying no electrical charge.



have proved themselves to be reliable over a number of years, and although each has certain disadvantages they are still greatly used to-day; among these are casein-lime mixtures and casein-ammonia mixtures which form emulsions relatively stable to hard waters, and blood albumin which is used to facilitate emulsification of tank-mix sprays in which the ingredients are added separately to the tank of the spray machine and emulsified by agitation immediately prior to application. Certain solids, for instance fine clay, will also act as emulsifiers but they have had only limited application.

Although some of the most efficient insecticides, such as oil, are water-immiscible, they can nevertheless be used with water as a carrier providing they are dispersed through the water phase on fine droplets to form an emulsion. Emulsifying agents promote this dispersion and ensure stability by modifying the forces at the interface of the two liquids in such a manner that subsequent coalescence of the droplets is prevented. Many of the substances which possess this particular property are composed of large molecules, often with a long chain structure, each of which presents dual characteristics in that part of it is attracted to the water phase while the remainder is water repellent; because of the opposing forces which come into play, the emulsifier molecules orientate themselves at the water-oil interface, and act as if they formed a film or envelope surrounding each droplet and preventing coalescence. By the choice of a suitable emulsifier, it is possible to obtain either an oil-in-water emulsion or the reverse in which the water is dispersed in the oil phase. For the greater majority of spray treatments the oil-in-water emulsion is applied but for some purposes the inverted type has been successfully used for the application of protective stomach poisons, such as lead arsenate, when it is desired to build up a heavy deposit on the plant surface.

One of the prime requisites of the majority of sprays is that intimate contact should be made with the plant or insect surface, and that an even and unbroken deposit or film of the toxicant should be laid down. As plant and insect surfaces are highly water-repellent, the spray fluid tends to remain as drops rather than to spread out as a continuous film thus leaving spots of deposited toxicant irregularly dispersed. Certain additives known as wetting and spreading agents aid





**Fig. 7.**—Dusting machine mounted on a high clearance tractor for use on seed crops for the control of pollen beetle or mustard bug. Photograph by courtesy of Pest Control Ltd.

the formation of a continuous film and the intimate contact with water-repellent surfaces; they are surface-active chemicals similar in structure to the emulsifiers—in fact, wetters and spreaders all have some emulsive properties. Broadly speaking, the molecular structure of these bodies is such that part of the molecule has an affinity for water while the remainder is repelled by it; in a manner analogous to the action in emulsification, the molecules of the additive orientate themselves at the sur-

face of the drop and so modify the surface tension and the liquid-solid interfacial tension that intimate contact is promoted and the liquid creeps over the surface to form an even film. Many of the synthetics which have been primarily developed as emulsifiers and detergents are used as wetting and spreading agents; amongst them are sulphonated oils, the higher sodium alkyl sulphates and other surface-active materials. Adequate reviews of them have been given by Martin<sup>3</sup> and elsewhere.

Stickers are included in sprays carrying protective stomach poisons and are designed to improve the retention of the deposit, particularly with regard to “weathering” in which leaching by rain and dew play an important part. In comprehensive studies on the behaviour of this type of additive, Fajans and Martin<sup>14</sup> observed that while certain spreaders which are soluble with difficulty in cold water, or which form insoluble residues on drying, enhance the tenacity of the toxic deposit and thereby also act as stickers, other adjuvants which are readily



soluble, for instance, sulphite lye, promote the leaching out of the deposit and so reduce tenacity. Many of the additives specifically included as stickers are true adhesives which firmly fix the toxicant to the plant surface; examples of these are flour and gums. Probably the most widely used sticker to-day is petroleum white oil which is applied in the United States and other countries in conjunction with lead arsenate or cryolite for the control of the codling moth.

Dispersing agents aid dispersion and delay sedimentation in those sprays which consist of solid particles of toxicant suspended in water. Protective colloids such as gelatine, glue and various gums, will perform this function. It is thought that their mode of action is twofold and that sedimentation is delayed partly by the increase in particle size resulting from their adsorption at the solid surface, and partly by the increase in viscosity their presence confers on the suspending liquid. Other agents, which are not colloids, probably act in a similar manner, but disperse aggregations of amorphous particles; as their action depends on surface activity, many spreaders are suitable additives for this purpose.

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## CHAPTER IV

### FUMIGATION

THE idea of utilizing poisonous gases to rid the home of annoying pests was well known to the ancients, for Homer in the *Odyssey* mentions the use of burning sulphur for disinfestation and Hippocrates likewise refers to the practice of fumigation by burning various gums and resins. Little headway could be made in this direction until the science of chemistry was able to provide efficient gases and technique to enable them to be used with safety; to-day, fumigation is a highly developed science and at least one of the common gases employed, hydrogen cyanide, has become universally known through the medium of detective fiction.

The fumigants employed are all toxic to man and animals in a greater or lesser degree and although in theory it might be possible to fumigate uncovered standing crops utilizing heavy gases, in practice this cannot be done because of the difficulties in controlling them. Fumigation is therefore limited to the destruction of insects in confined places which may be ordinary buildings and warehouses temporarily sealed to prevent gas leakage, chambers specially designed for this practice or temporarily erected tents over trees and crops.

Probably the most important aspect of fumigation is that which concerns the control of insect pests attacking stored products such as grain, dried fruits and tobacco, which can suffer very material losses from the depredations of these pests. The necessity of conserving food stocks in the second world war provided an impetus to the study of fumigant gases and the best method of utilizing them, and possibly the greatest development has been achieved by Page<sup>1</sup> and his co-workers in devising methods by which the distribution of the gas in the fumigated material can be ascertained.

#### Action of fumigants on insects

Insects breathe by means of air tubes—the trachea—ramifying



throughout the body with access to air through openings on the surface of the body—the spiracles. The air passes from the trachea to tubes of lesser diameter—the tracheoles—and enters into solution with the cell cytoplasm by diffusing through the thin walls of the tracheoles.<sup>2</sup> Diffusion of the air through the respiratory system is assisted by movements of the abdomen and thorax of the insect.

Certain enzymes govern the oxidation and respiration of living cells and according to Shafer<sup>3</sup> insects are not killed unless the amount of fumigant present is enough to interfere seriously with the activity of one or more of these enzymes. Shephard<sup>4</sup> reported that fumigants exert their toxic action by penetrating the respiratory system but they are not necessarily respiratory poisons. According to Blyth,<sup>5</sup> the vapour of nicotine paralyses the respiratory tract, causing death. McIndoo,<sup>6</sup> also, considered that nicotine used as a fumigant kills by causing paralysis, the vapour condensing in the trachea.

Increase or decrease in the rate of respiration influences the susceptibility of insects to the fumigant and the three important factors affecting the respiratory rate are; the carbon dioxide and the oxygen content in the fumigation chamber, and the temperature. Brinley and Baker<sup>7</sup> noticed that some insects closed their spiracles when placed in sublethal concentrations of hydrogen cyanide and that the addition of a small quantity of methyl acetate to the liquid hydrogen cyanide caused the spiracles to remain open. Hazelhoff<sup>8</sup> called attention to the effect of carbon dioxide on respiratory movement and tracheal valve control and suggested that, in fact, carbon dioxide might have the same effect when used with hydrocyanic acid as did the methyl acetate. Cotton and Young<sup>9</sup> reported that the toxic action of a number of fumigants was accelerated by the addition of carbon dioxide. The use of carbon dioxide with inflammable fumigants has the added advantage of reducing the fire hazard.

Cotton<sup>10</sup> showed that insects were more susceptible to the fumigant when the oxygen content of the chamber was reduced below 7 per cent. Moore and Carpenter<sup>11</sup> observed that they were more susceptible when nitrogen was absent. It was found in the fumigation of fruit trees that red scale was more susceptible to the fumigant at lower temperatures and a higher percentage mortality was produced at 10° C. than at 24° C.



or 32° C.<sup>12, 13</sup> On the other hand, black scale shows greater tolerance to hydrocyanic acid at lower temperatures.<sup>14</sup>

### Factors influencing the efficiency of fumigants

The diffusion rate of a fumigant is dependent upon its molecular weight. Theoretically, therefore, a fumigant with a low molecular weight should diffuse more rapidly than one with a higher molecular weight. In an empty building, this does happen in practice provided there are no disturbing factors such as a draught inducing a higher concentration of fumigant at one part of the building. It has been shown that this uniform distribution occurs with hydrocyanic acid<sup>15</sup> for instance. This, however, does not obtain in a filled or partly filled warehouse. In addition, a higher dosage is required when fumigating a building containing stored produce as a proportion of the fumigant is absorbed by the commodity. The amount absorbed varies with the commodity, the temperature and the gas used. It has been found<sup>16</sup> that the amount of hydrocyanic acid required in vacuum fumigation to give a 100 per cent. kill at 80° F. of insects in bagged flour had no effect on them at 50° F.

Lindgren and Shephard<sup>17</sup> reported that differences in humidity, in some cases, affect the toxicity of some fumigants to different life stages of the confused flour beetle (*Tribolium confusum*). In general, however, variation in humidity does not affect the toxicity of fumigants. It has been reported<sup>18</sup> that in tent fumigation of fruit trees a higher percentage mortality is produced as the humidity increases. This may have been due to the fibres of the tent being swollen by the moisture and thereby increasing the gasproof qualities of the cloth and Swain and Buckner<sup>19</sup> found that in an airtight chamber a higher percentage kill results at lower temperatures.

Fumigants with a high vapour pressure can be used more effectively at lower temperatures than those with a lower vapour pressure. In fumigating a building, it is an advantage to build up a maximum concentration as rapidly as possible and when using a fumigant of low vapour pressure, this naturally presents some difficulties in structures which are not gas-tight.

Vacuum fumigation is used more extensively in America than in this



country. In this method a gastight chamber is used. These vary in shape and size depending upon the nature of the material and the amount to be fumigated. The air is withdrawn from the chamber by means of a vacuum pump and replaced by a fumigant. More rapid penetration of the material is possible when this method is used than under atmospheric pressure. Thus the insects are reached and killed more rapidly and due to the lower oxygen content they are more susceptible to the fumigant. Vacuum fumigation requires one to three hours as against ten to twenty-four for atmospheric fumigation. The fumigant can be removed from the treated produce by creating a vacuum in the chamber and then permitting air to enter ("washing with air").

Tent fumigation is used extensively in citrus-growing areas for the control of scale pests. The tree, or row of trees, is covered by a gasproof tent into which the fumigant is introduced. The material used in the construction of the tent is usually a duck or drill of adequate strength and tightness of weave. Quayle<sup>18</sup> has given a detailed account of this type of fumigation.

## THE COMMON FUMIGANTS

### Hydrocyanic Acid HCN

Hydrocyanic acid is one of the most well known and commonly used fumigants and was discovered by Scheele in 1782. It is extremely toxic to warm-blooded animals and requires extremely careful manipulation and use.

Hydrocyanic acid is a colourless gas with a definite almond-like odour, boiling point  $25.7^{\circ}\text{C.}$ , specific gravity  $\frac{20^{\circ}}{d\ 4^{\circ}}\ 0.699$ , vapour pressure  $738.8\text{ mm. at }25^{\circ}\text{C.}$ , its vapour density is almost identical with that of air, one gramme occupying 900 mil. at  $26.6^{\circ}\text{C.}$

Coquillett<sup>20</sup> first employed hydrocyanic acid against scale insects on citrus trees. He generated the gas by the pot method, adding sulphuric acid ( $1\frac{1}{2}$  pints) to water (3 pints) and then adding potassium cyanide (1 lb.) to the diluted acid. The potassium cyanide was later replaced by the cheaper sodium cyanide. According to Mallis<sup>21</sup> the amount of hydrocyanic acid generated from the above mixture is sufficient to



fumigate 1,000 cubic feet of air space. Miles<sup>22</sup> recommends for use in glasshouses,  $\frac{1}{8}$  to  $\frac{1}{4}$  oz. of sodium cyanide (depending upon the state of the structures) in a proportional amount of diluted acid per thousand cubic feet. Dean and co-workers<sup>23</sup> have described the use of the pot method for the fumigation of flour mills.

Calcium cyanide liberates hydrocyanic acid on exposure to air and is used, in fact, as a source of the gas and obviates the possibility of accident or danger in handling the acid. The use of calcium cyanide in mills and glasshouses has been fully described elsewhere.<sup>21,22</sup>

Hydrocyanic acid can also be used in the form of the liquified gas absorbed in kieselguhr or fibre discs—Zyklon and Discoids, each of which contains a definite quantity of the gas.

Liquid hydrocyanic acid is used in mills, warehouses and tent fumigation for the control of pests on citrus trees.

### **Chloropicrin $\text{CCl}_3\text{NO}_2$**

Chloropicrin was used as a war gas in the first world war by the Russians (in 1916). The gas causes intense irritation of the eyes and induces vomiting at relatively low concentrations. Chloropicrin is also known as “Klop” (Germany), “Aquinite” (France), and “PS” (America).

Chloropicrin is a colourless or slightly yellowish liquid, first prepared by Stenhouse in 1848 and has boiling point  $112^\circ \text{C.}$ , specific gravity  $\frac{0^\circ}{4^\circ} 1.692$ , melting point  $69^\circ \text{C.}$ , vapour pressure 23.9 mm. at  $25^\circ \text{C.}$ , vapour density 5.7. It is used extensively (alone or admixed with carbon tetrachloride or trichlorethylene) in America where its main use is as a fumigant for the grain and milling industries and to a lesser extent for household fumigation by pest control operators. Chloropicrin is extremely toxic to insects and at normal working temperatures is non-inflammable and non-explosive. The liquid is difficult to vaporize, rather slow in action on insects, and must be aired out thoroughly from flour after fumigation as chloropicrin can inhibit yeast fermentation.

### **Ethylene Dichloride, $\text{C}_2\text{H}_4\text{Cl}_2$**

Ethylene dichloride is a colourless liquid, boiling point  $83.5^\circ \text{C.}$ ,



melting point  $-36^{\circ}\text{C.}$ , vapour pressure 79.6 mil. at  $25^{\circ}\text{C.}$ , specific gravity  $\frac{20^{\circ}}{d\ 4^{\circ}}$  1.257, lower and upper limits of inflammability 6.2 per cent. and 15.9 per cent. Used in the proportion of 75 per cent. by volume of ethylene dichloride and 25 per cent. by volume of carbon tetrachloride a satisfactory non-inflammable mixture can be obtained which is a satisfactory fumigant. This mixture has been used in flour mills and for the treatment of stored grain and does not affect the germinating properties of grain.

Ethylene dichloride is less toxic to human beings than are some of the fumigants in common use (*e.g.* hydrocyanic acid) but has an anaesthetic action and care must be exercised to avoid undue exposure to the vapour.

### Ethylene Oxide $(\text{CH}_2)_2\text{O}$

Ethylene oxide is a colourless liquid, boiling point  $11^{\circ}\text{C.}$ , specific gravity  $\frac{7^{\circ}}{d\ 4^{\circ}}$  0.887, vapour pressure 493.1 mm. at  $0^{\circ}\text{C.}$ , 112.5 lb. are required to saturate 1,000 cubic feet at  $25^{\circ}\text{C.}$  The vapour is inflammable, the lower and upper limits of inflammability being 3 per cent. and 80 per cent. by volume.

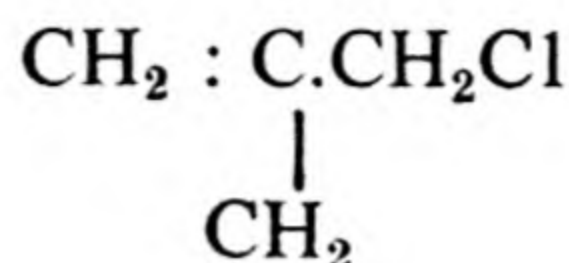
In this country, ethylene oxide is used in warehouses containing a wide range of produce and in barges. This fumigant is used generally in conjunction with carbon dioxide and the mixture of ethylene oxide (90 per cent.) and carbon dioxide (10 per cent.) is sold under the name "Etox". Ethylene oxide vaporizes with great rapidity on exposure to air and can be used at relatively low temperatures. It is slower in action than hydrocyanic acid and has good ovicidal properties. It should not be used for the treatment of grain intended for seed as it seriously affects germination.

### Methallyl Chloride

Methallyl Chloride is one of the newer fumigants which has not, as yet, been used very extensively but appears to have many desirable properties. Its development has been due largely to Briejèr<sup>24</sup> who first



carried out laboratory tests and then followed these up by large-scale trials. It is used as a fumigant in Holland and to a lesser extent in the United States.



Methallyl Chloride is a colourless liquid with a boiling point of 72° C. and readily vaporizes in the open at temperatures above 14° C. The liquid is irritant if spilled on the skin but can be removed by washing.

Briejèr demonstrated that methallyl chloride vapour is toxic to all the common stored-product pests at dosages which can easily be obtained by exposing the liquid in open trays and that these concentrations are below those which form explosive mixtures with air. He investigated the dosage time factor, penetration of the vapour and its absorption by various commodities and, by correlating these with the toxic effect on the insects he was able to state recommended dosages for varying treatment times according to the material being fumigated and the type of building being used. He found the vapour penetration sufficient to kill pests in bagged grain but concluded that for large silos it would be necessary to pump the gas through the wheat to effect complete penetration. The ventilation time for dispersal of the vapour after treatment lies between six and twenty-four hours. The operators should wear gas-masks but the toxicity to mammals is considerably less than that of ethylene oxide and is only of the same order as that of carbon disulphide; the irritating odour serves as a clear warning of its presence. Application is either by volatilization from open trays or by atomization through nozzles, using compressed air as a propellant.

Briejèr investigated, first in the laboratory and then by observation of commercial practice, the effect of the gas on a large number of those commodities subject to pest infestation; no change in taste or appearance was recorded from such diverse materials as grain, dried fruit, cocoa and coffee beans, nuts, furs and furnishings. He does not recommend its use on potatoes or flour although flour mills have been successfully fumigated without treating the stock.



**Methyl Bromide, CH<sub>3</sub>Br**

Methyl bromide is widely used as a fire extinguisher and has been found superior to other products for extinguishing fires in aircraft power plants.<sup>25</sup>

At ordinary temperatures methyl bromide is a gas and is about 3.3 times as heavy as air, the liquid form is colourless. Methyl bromide has boiling point 4.6° C., specific gravity  $\frac{0^\circ}{d\ 0^\circ}$  1.73, vapour pressure 760 mm. at 25° C.

Le Goupil<sup>2</sup> first reported the insecticidal properties (which are comparable with those of hydrocyanic acid and ethylene oxide) of methyl bromide. The chemical is toxic to man and the effects are cumulative and care must therefore be taken in the use of this fumigant. At low concentrations, methyl bromide is almost odourless but traces can be detected by means of a halide leak detector. This consists of a copper cone or tube heated by an alcohol or acetylene flame, a sample of the air to be tested is passed over the red hot copper tube or cone and from the colour of the flame produced the concentration of the methyl bromide can be determined as shown in the following table:

Parts CH <sub>3</sub> Br per million by volume	Pounds CH <sub>3</sub> Br per 1,000 cubic feet	Flame colour
0	0	Almost invisible
40	0.010	Rather faint green
60	.014	Moderate green
100	.024	Moderate green
130	.031	Strong green; slightly blue at edges
180	.043	Strong green; rather blue
240	.058	Strong blue-green
360	.086	Strong blue-green
800	.192	Strong blue

The American forces used methyl bromide as a lousicide during the second world war. The troops were issued with relatively gas-tight bags, large enough to hold one soldier's uniform and blankets, and the



methyl bromide introduced by breaking a glass ampoule containing the fumigant in a pocket in the bag. The period of fumigation was forty-five minutes and the clothes were ready to wear after five minutes' airing. For larger-scale fumigation, portable mobile vaults were used.<sup>26</sup>

Methyl bromide has been found of great value in America for the treatment of flour mills, warehouses, goods wagons and for the fumigation of plant material being moved through quarantined areas.

### **Trichloroacetonitrile $\text{Cl}_3\text{C} \cdot \text{CN}$**

Trichloroacetonitrile, which possesses many desirable characteristics as a fumigant, was developed and tested on a practical scale in Germany for the disinfestation of dwelling-houses and warehouses. Bovingdon and Coyne<sup>27</sup> pursued the investigation in England and it is from their publication that this brief account is largely drawn.

Trichloroacetonitrile is a liquid with a boiling point of  $85^\circ \text{C}$ . and is easily vaporized into a gas of vapour density 4.95 (air = 1). It is non-inflammable, does not attack stored products such as dried fruit or harm furnishings and clothes but it can cause discoloration of iron and steel. Its toxicity to man is of the same order as that of ethylene oxide but it is strongly lachrymatory and thus gives warning of its presence at concentrations as low as 5–10 mg./cu.m. Because of its low absorption by materials the gas is readily dispersed after treatment by airing and no trace can be detected in treated bulk grain after forty-eight hours' ventilation.

Bovingdon and Coyne investigated the action of this fumigant against grain pests both on a laboratory scale and in trials using bulk grain and demonstrated that its efficiency was similar to that of ethylene oxide both as regards dosage and time of exposure. The losses due to absorption were not high but no chemical estimation was made of any residues resulting from possible reactions of the trichloroacetonitrile within the grain. Tests on treated grain showed that germination was only slightly affected at doses which might be used in practice, while both the vitamin  $\beta$  and riboflavin content were unchanged.

The same workers showed that the toxicity of the gas to houseflies was increased by the addition of 10 per cent. or more by volume of



carbon dioxide. They conclude that trichloroacetonitrile possesses definite possibilities as a fumigant for stored grain, dried fruit and household disinfestation but that its phytocidal action on growing plants probably precludes its use against plant pests.

Further investigations on the use of trichloroacetonitrile are in progress but it seems possible that its action on iron and steel fittings, especially at high humidities, may prove a serious disadvantage to its development.

### Miscellaneous Fumigants

Roark and Cotton<sup>28</sup> have reported the results obtained in tests with more than 300 aliphatic compounds as fumigants. Shephard and co-workers<sup>29</sup> have examined a number of halogen and sulphur-substituted organic compounds.

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## CHAPTER V

### NICOTINE

THE use of nicotine as an insecticide dates back as far as 1690<sup>1</sup> when a tobacco wash was used for the control of the pear lace bug on pear trees in France. The insecticidal uses of tobacco were known in England in 1764<sup>2</sup> and in that year Peter Colinson wrote to an American botanist recommending the use of an aqueous tobacco extract for the control of the plum curculio. McIndoo<sup>1</sup> reported that tobacco powder and the aqueous extract of tobacco were used in England for the control of red spider and aphids in 1773. As an insecticide, tobacco was first used in America in 1814<sup>1</sup> against sucking insects. In 1773 tobacco was used as a fumigant,<sup>1</sup> smoke being obtained by the action of a heated iron pipe on tobacco. By 1890 tobacco extracts were commonly mentioned in the literature; however, the entomological investigation of nicotine did not commence until 1916.<sup>1</sup>

#### Chemistry of Nicotine

Nicotine is the principal alkaloid found in tobacco where it occurs as the salts of citric and malic acids. The alkaloid was discovered in 1828 by Posselt and Reiman<sup>3</sup> who isolated it from *Nicotiana tobacum*, *Nicotiana rustica*, *Nicotiana macrophylla* and *Nicotiana glutinosa*. Penner<sup>4</sup> established its structure in 1893 and the alkaloid (3-(1-methyl-2-pyrrolidyl) pyridine) was synthesized in 1904 by Pictet and Rotschy.<sup>5</sup>

The source of nicotine (named after Jean Nicot who introduced the plant into Europe in 1560) is the tobacco plant of which there are about a hundred species but only two are of commercial importance. *Nicotiana tobacum* is the ordinary tobacco of commerce and provides nearly all the cigarette, cigar and pipe tobacco. *Nicotiana rustica* is a coarser species and contains the highest proportion of nicotine of all the nicotiana species.<sup>2</sup> Experimental cultivation of this species in Britain, America and South Africa as a source of the alkaloid showed that the nicotine content depends to a great extent on the climate and condition of the soil. The nicotine content of *Nicotiana rustica* cultivated in



Kenya averages 9 per cent. (a maximum of 20 per cent. being obtained). That cultivated in Russia as a source of the alkaloid varies from 2 to 8 per cent. and in Germany, a nicotine content of up to 15 per cent. has been obtained.<sup>2</sup>

Nicotine is found in all parts of the plant and Klein and Herndlhofer,<sup>6</sup> by microchemical methods, showed that the greatest concentration of the alkaloid is in the leaves and roots.

In addition to nicotine eleven other alkaloids have been found in tobacco<sup>2</sup>:

Nicotimime	...	...	$C_{10}H_{14}O_2$	<i>l</i> -N-methyl Anatabine	$C_{11}H_{14}N_2$
Anabasine	...	...	$C_{10}H_{14}O_2$	Nicotyrine	... $C_{10}H_{10}N_2$
<i>N</i> -methyl anabasine			$C_{11}H_{16}N_2$	Nicotelline	... $C_{10}H_8N_2$
<i>iso</i> Nicotine	...	...	$C_{10}H_{12}N_2$	2 : 3'-Dipyridyl	... $C_{10}H_8N_2$
Anatabine	...	...	$C_{10}H_{12}N_2$	Nornicotine	... $C_9H_{12}N_2$
				Nicotine	... $C_8H_{11}N$

but only two of them appear to be of interest as insecticides.

Nicotine is an almost colourless liquid, boiling point  $247^\circ C.$ , specific gravity 1.018 at  $10^\circ C.$ , soluble in water, volatile and does not scorch plants (non-phytotoxic). On ageing, nicotine turns brown, taking on the odour of tobacco. The alkaloid is prepared by adding alkali to a filtered concentrated aqueous extract of tobacco (waste leaf and stems from tobacco factories generally used) and recovering the nicotine by steam distillation.

Compounds having an asymmetric carbon atom exist in two forms and are optically active, rotating the plane of polarized light in opposite directions and known as the laevorotatory (*l*) and dextrorotatory (*d*) forms. A mixture of equal quantities of the two forms does not, of course, rotate the plane of polarized light and such a mixture is called a conglomerate or racemic mixture (*dl*-form).

The naturally occurring alkaloid,  $\beta$ -nicotine, is the laevorotatory form and  $\alpha$ -nicotine is the dextrorotatory form.

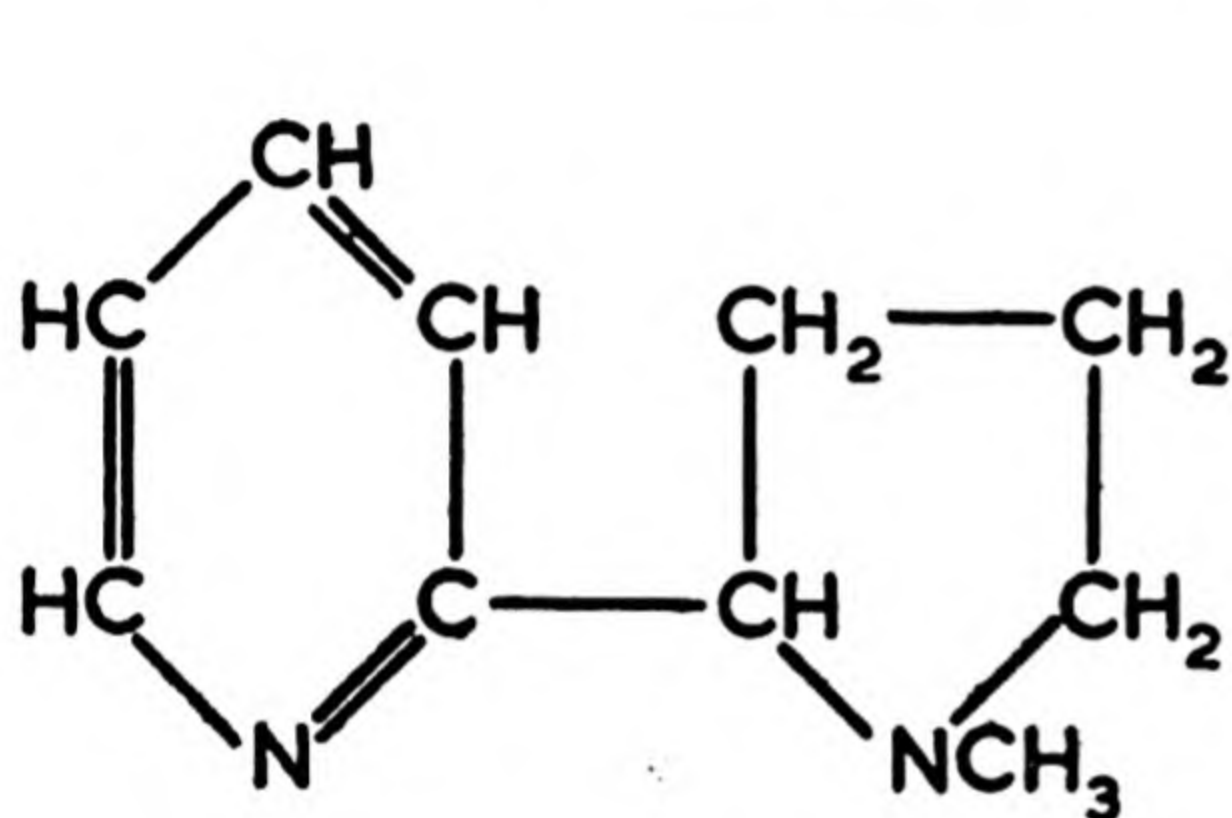
Ageing does not appear to affect the insecticidal action of nicotine. McDonnell and Young<sup>7</sup> reported that on exposure to air nicotine sulphate solutions became concentrated to about 45.5 per cent nicotine due to evaporation but with little or no loss of nicotine. On the other



hand, solutions of free nicotine under the same conditions lose in addition to water 10–17 per cent of the nicotine originally present and reach equilibrium at a concentration of 89 per cent nicotine.

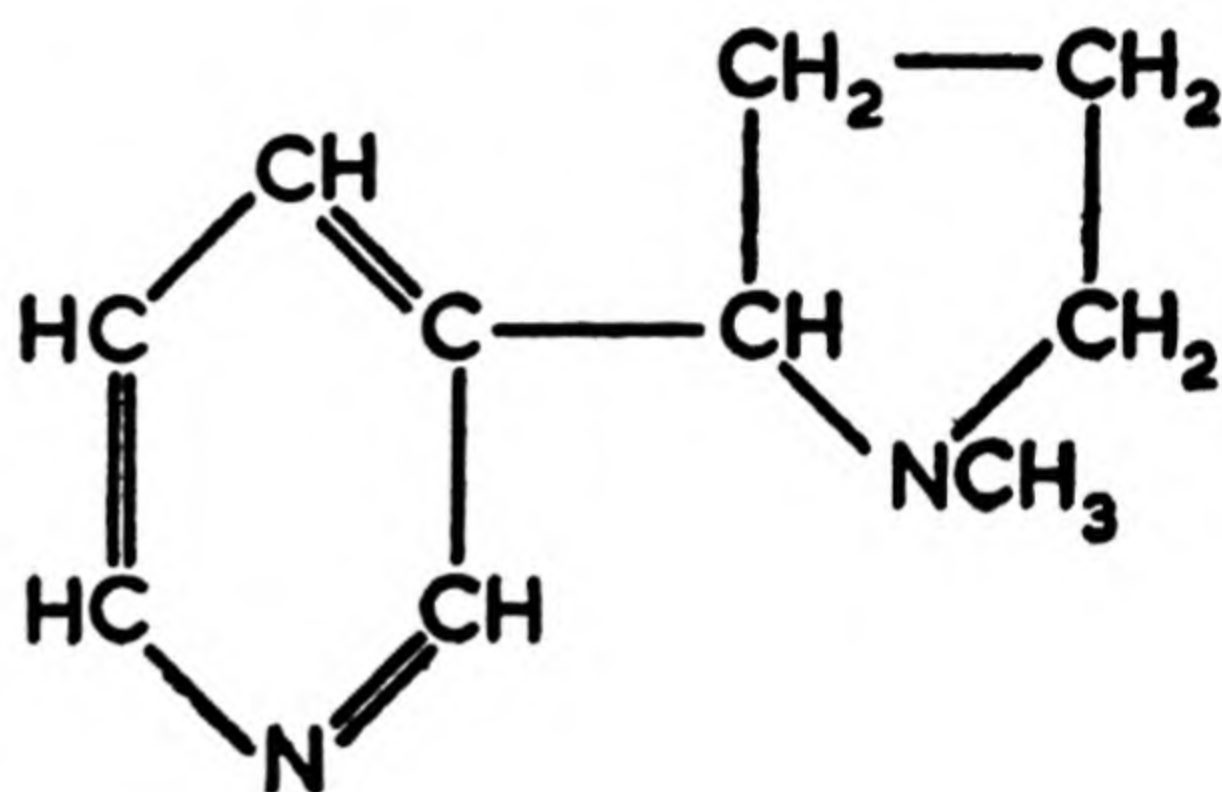
### Mode of action

According to McIndoo,<sup>8</sup> nicotine spray solutions do not pass into the tracheae nor do they penetrate the insects' integument; the fumes from nicotine used as a fumigant and the vapour from nicotine spray pass into the tracheae and are widely distributed to all the tissues. He



$\alpha$  NICOTINE

Fig. 8



$\beta$  NICOTINE

Fig. 9

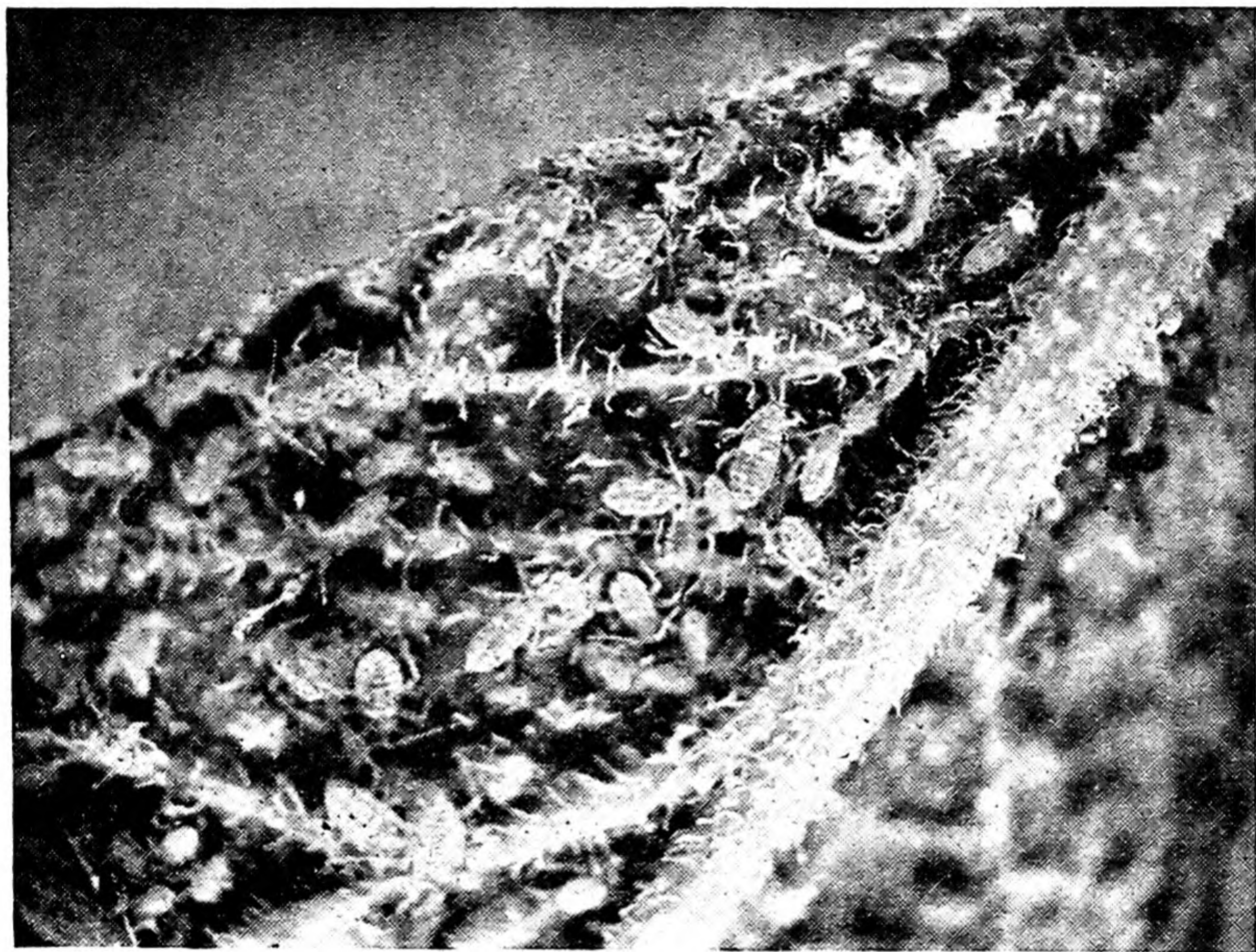
concluded that regardless of the method of application, nicotine kills by paralysis, which in insects travels along the ventral nerve cord from the abdomen to the brain. De Ong<sup>9</sup> stated that caterpillars that may ingest nicotine by the mouth are exceptions to the fumigant action of nicotine.

The median lethal dose\* of nicotine as a contact spray for wingless mature bean aphid (*Aphis rumicis*) was shown by Craig and Richardson<sup>10</sup> to be 0.04 mg. per 100mil. for the *l*-form and 0.12 for the *dl*-form. Richardson and co-workers<sup>11</sup> found solutions of *l*- $\beta$ -nicotine to be nearly twice as toxic to the bean aphid as the corresponding solutions of the *dl*-form. De Ong<sup>9</sup> reported that nicotine in the free state is

\* Median lethal dose, the dose necessary to give a 50 per cent. mortality.



readily volatilized and is much more toxic than when combined with acids to form non-volatile salts. Richardson and Shephard<sup>12</sup> studied the toxicity of nicotine in aqueous solutions, using larvae of the mosquito (*Culex pipiens*) as test insects. They found that the speed of toxic action of nicotine, pyridine and methyl pyridine in aqueous solutions was



**Fig. 10.**—Mealy plum aphids on underside of plum leaves. *A Shell Photograph.*

related to the concentration of the undissociated molecules. It appeared that toxicity resulted from the molecules entering the body of the insect through the wall of the alimentary tract. Their results showed that the volatility of nicotine is not the only factor since the free nicotine in solution was 5–7 times more toxic than nicotine sulphate of equivalent concentrations in actual nicotine.

Nicotine insecticides are recommended mainly for soft-bodied insects



such as aphids, thrips, leafhoppers, mushroom flies, etc. Nicotine has also been used successfully against a number of mites including red spider (*Tetranychus* spp.). McIndoo<sup>1</sup> has summarized the insecticidal uses of nicotine.

### Methods of use

The use of nicotine preparations has been investigated with a view to compounds of the alkaloid replacing lead arsenate for the control of codling moth. For this purpose, the volatility of nicotine is a disadvantage and a fixed nicotine is required. Preliminary investigations<sup>13</sup> showed that nicotine tannate possessed considerable toxic properties. Tests against second brood codling moth gave the following results, nicotine tannate gave 73.2 per cent. of the total fruit free from codling moth injuries compared with 57.5 per cent. of the fruit from trees subjected to the standard lead arsenate spray treatment. The nicotine tannate treatment is more expensive but this is offset by the higher percentage of clean fruit. De Sellem<sup>14</sup> found that nicotine possessed ovicidal properties against the eggs of codling moth.

Nicotine dusts were first used in 1917. Dusts consist usually of finely powdered fuller's earth, kaolin, hydrated lime, dolomite, calcium carbonate, gypsum, sulphur and other absorbent materials in which free nicotine or nicotine sulphate is incorporated. It was found that the rate of volatilization of the nicotine from dusts depended upon whether nicotine or nicotine sulphate was used, the chemical and physical nature of the absorbent material and the type of container. Thatcher and Streeter<sup>15</sup> divided fillers or carriers for nicotine sulphate into three groups:

1. Colloidal substances such as kieselguhr and kaolin that tend to prevent volatilization.
2. Crystalline substances such as gypsum that are inert.
3. Active, all the common hydroxides and carbonate that change the nicotine sulphate into the more volatile free nicotine.

Nicotine sulphate is used to a greater extent for the incorporation of nicotine in dusts.

The rate of loss of nicotine from nicotine sulphate dusts prepared with kaolin, kieselguhr, talcum, plaster of Paris, calcium hydroxide and



calcium carbonate follows the order in which the carriers are listed. Nicotine is lost much more rapidly from dusts made with free nicotine than for those prepared from nicotine sulphate. The effect of the carriers is much about the same in both cases.

De Ong<sup>9</sup> reported that the toxicity of nicotine solutions is related to their conversion to the free alkaloid. The volatility of nicotine sulphate solutions was increased by varying the hydrogen-ion concentration of the solutions as shown in Table 1.

TABLE 1

*Effect upon toxicity of adding alkali to nicotine sulphate (de Ong)*

Spray	pH	Mortality of aphids per cent.
Nicotine sulphate 1-1,000 .	6.5	53.6
Same with 2.4 mil. N/1 NaOH .	6.7	49.7
Same with 4.8 mil. N/1 NaOH .	7.2	60.9
Same with 7.2 mil. N/1 NaOH .	7.8	65.4
Same with 9.6 mil. N/1 NaOH .	8.2	76.5

Moore<sup>16</sup> showed that the efficiency of free nicotine spray may be increased by as much as 50 per cent. by the addition of soap. It was found, however, that many commercial nicotine-soap preparations lost nicotine during storage. Investigation showed<sup>17</sup> that hard sodium soaps containing free nicotine deteriorated rapidly. This was not the result of volatilization of the nicotine but was due to the formation of an insoluble resinous compound which bound the nicotine and was apparently dependent upon the physical condition of the soaps. Soft sodium and potassium soaps retained the nicotine for at least four years.

It was reported<sup>18</sup> later that the loss of nicotine from soap-nicotine products made from non-drying oils (e.g. oleic acid, stearic acid) and stored so that air was not excluded was due to volatilization of the



nicotine, no insoluble condensation product being formed. Under the same conditions but using soaps made from drying oils (e.g. fish oils, linseed oil) the loss was due mainly to oxidation, the nicotine and part of the fatty acids forming a condensation product of indefinite composition.

Garman<sup>19</sup> reported that the toxicity of nicotine sulphate was increased by 8–27 per cent. by the addition to the aqueous solutions of gum karaya and a wetting agent such as sodium oleate. Sharp<sup>20</sup> showed that the addition of agar-agar to a nicotine sulphate spray trebled its effectiveness against the pea aphid (*Illinoia pisi*). Both agar-agar and gum karaya are unsatisfactory for general use owing to the difficulty of dispersion. Alcohol and light mineral oils materially assist the dispersion of gum karaya, and agar-agar is best dispersed by adding boiling water to the gum.

Austin and co-workers<sup>21</sup> in preliminary tests of Tinocine D (a long chain nicotinium bromide) reported that its insecticidal properties did not appear to be affected by the change in the molecular structure of the alkaloid.

Hansberry and Norton<sup>22</sup> examined the following compounds for toxicity to the bean aphid:

1. Nicotine alginate, 7.9 per cent. nicotine.
2. Nicotine araskat, 21.48 per cent., apparently a compound of nicotine with alkyl phenyl benzene sulphonic acid.
3. Nicotine caseinate, 20.64 per cent. nicotine.
4. Nicotine humate, 32.7 per cent. nicotine.
5. Nicotine laurate, 44.7 per cent. nicotine.
6. Nicotine oleate, 36.5 per cent. nicotine.
7. Nicotine lineolate, 36.6 per cent. nicotine.
8. Nicotine stearate, 36.3 per cent. nicotine (a waxy solid).
9. Nicotine naphthenate, 36.1 per cent. nicotine (prepared from naphthenic acid).
10. Nicotine peat, 10.05 per cent. nicotine.
11. Nicotine bentonite, 5.4 per cent. nicotine.
12. Nicotine silicotungstate, 10.12 per cent. nicotine.
13. Nicotine reineckate, 31.67 per cent. nicotine (reinecke salt is ammonium tetrathiocyano-diammono-chromate).
14. Nicotine resorcinol-formaldehyde, 21.5 per cent. nicotine.
15. Nicotine cuprocyanide, 60 per cent. nicotine.
16. Dodecyl nicotinium iodide, 36 per cent. nicotine.
17. Dodecyl nicotinium di-iodide, 22 per cent. nicotine.
18. Dodecyl nicotinium bromide, 40 per cent. nicotine.
19. Dodecyl nicotinium di-bromide, 25 per cent. nicotine.



The nicotine humate was soluble in water with difficulty, forming a dense black solution with little wetting and spreading ability. The nicotine stearate did not dissolve completely but dispersed fairly well in warm water. Nicotine silico-tungstate was the least soluble of the compounds tested. The dodecyl nicotinium preparations were all viscous, tarry materials; they had excellent wetting and spreading properties when dissolved or suspended in water with the aid of ethyl alcohol. Hansberry and Norton found that nicotine laurate, oleate, lineolate, stearate and naphthenate were about equal in toxicity to nicotine with sodium oleate as a spreader. Nicotine alginate, areskat, caseinate and humate were less toxic, the remainder having little or no toxicity to aphids. It was suggested that the group of fatty and naphthenic acid compounds was the most efficient because of the combined toxicity of the alkaloid and the acid, the increase in the efficiency being considered due to the wetting and spreading properties of the compounds and an unexplained synergistic action.

Mayer and Gahan<sup>23</sup> tested twenty-five nicotine compounds, comprising nicotine-metal compounds, nicotine salts of dye acids and the corresponding metal-nicotine double salts of the dye acids.

Test insects were large nymphs of the American cockroach (*P. americana*); termites (*Reticulitermes* spp adults and large nymphs); aphids (wingless aganic form) (*Macrosiphum ambrosia*); blister beetles (adults) (*Epicauta lemniscata*); and fourth instars of the following insects, cowpea weevils (adults) (*Callosobruchus maculatus*); bean leaf rollers (*Urbanus proteus*); cross striped cabbage worms (*Evergestis rimosalis*); greenhouse leaf tiers (*Phlyctaenia rubigalis*); Hawaiian beet webworms (*Hymenia fascialis*); melon worms (*Diaphania hyalinata*); pickleworms (*Diaphania nitadalii*); southern beet webworms (*Pachyzancla bipunctalis*); southern armyworms (*Prodenia eridania*); and common red spiders (*Tetranychus* sp.) together with the appropriate host plants for each, where applicable. Eleven types of plants were used in the phytotoxicity tests. The nicotine compounds were tested in comparison with those usually recommended for the control of the species of insect used. Mayer and Gahan summarized their results as follows: "Several types of tests were made to determine the insecticidal efficiency of twenty-five complex salts containing nicotine, usually combined



with a metal. In feeding tests with dusts diluted to approximately 5 per cent. nicotine content, at least six of the compounds were as effective against two to four species as was the recommended insecticide. These compounds, in descending order of effectiveness against from four to six species, were cupric dinicotine picrate, zinc dinicotine picrate, cuprous mononicotine thiocyanate, cupric dinicotine thiocyanate, nicotine paper yellow L (first fraction), and cuprous dinicotinammino thiocyanate. When these materials were applied to plants in dusts containing 15 per cent. of nicotine, little or no injury to the foliage was apparent. When tested as sprays, twelve of the compounds were as effective as the recommended insecticides against at least one of four species of insects on foliage sprayed with suspensions containing approximately 0.1 per cent. of nicotine. Of these twelve, only two, cuprous nicotine cyanide and cuprous dinicotinammino thiocyanate, caused no injury to foliage in spray suspensions containing 0.3 per cent. of nicotine. These are, therefore, the only compounds that can be recommended as safe to use in spray form. Most of the compounds that showed appreciable toxicity against lepidopterous larvae contained copper. Only two materials, cuprous mononicotine thiocyanate and cuprous dinicotinammino thiocyanate, were 100 per cent. effective in both dust and spray form. When dusted directly in Petri dishes and fed untreated foliage, melonworm larvae were only slightly affected by any of the materials, but the southern armyworm was affected by several where it was possible in each test for the larvae to eat some of the particles.

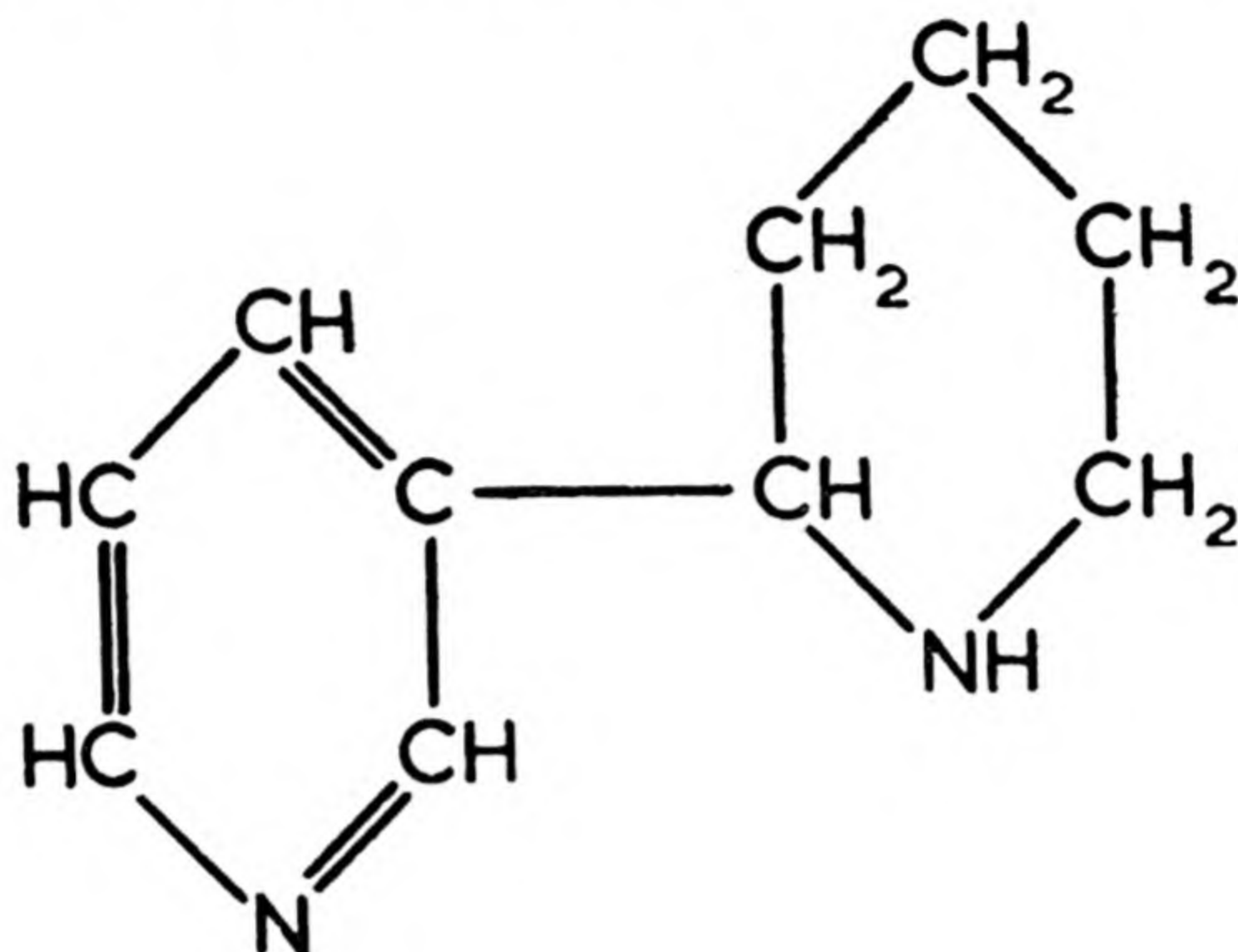
Cuprous nicotine cyanide killed all the large nymphs of the American cockroach in three days. None of the materials were effective against the cowpea weevil or against termites.

Smith and Goodhue<sup>24</sup> applied nicotine as an aerosol and as a combustible powder in a greenhouse and found that an application of 1.39 gm. per thousand cubic feet from the aerosol gave almost 100 per cent. kill of the green peach aphid (*Myzus persicae*) as compared with 68.5 per cent. from 1.27 gm. when applied as a combustible powder. They concluded that when dispersed as an aerosol only about one-half of the nicotine was required to produce a given mortality, in comparison with the amount of actual nicotine required when derived from a combustible powder.



## Compounds related to nicotine

Smith and co-workers<sup>25</sup> tested twenty-five dipyridyl derivatives and related compounds and found neonicotine to be the most toxic, comparing favourably with nicotine to which it is chemically similar.



NEONICOTINE (ANABASINE)

Fig. II

Neonicotine ( $\beta$ -pyridyl  $\alpha$ -piperidine) has the same empirical formula as nicotine, has boiling point  $280-281^{\circ}\text{C.}$ , is soluble in water in all proportions but is less volatile than nicotine in steam.

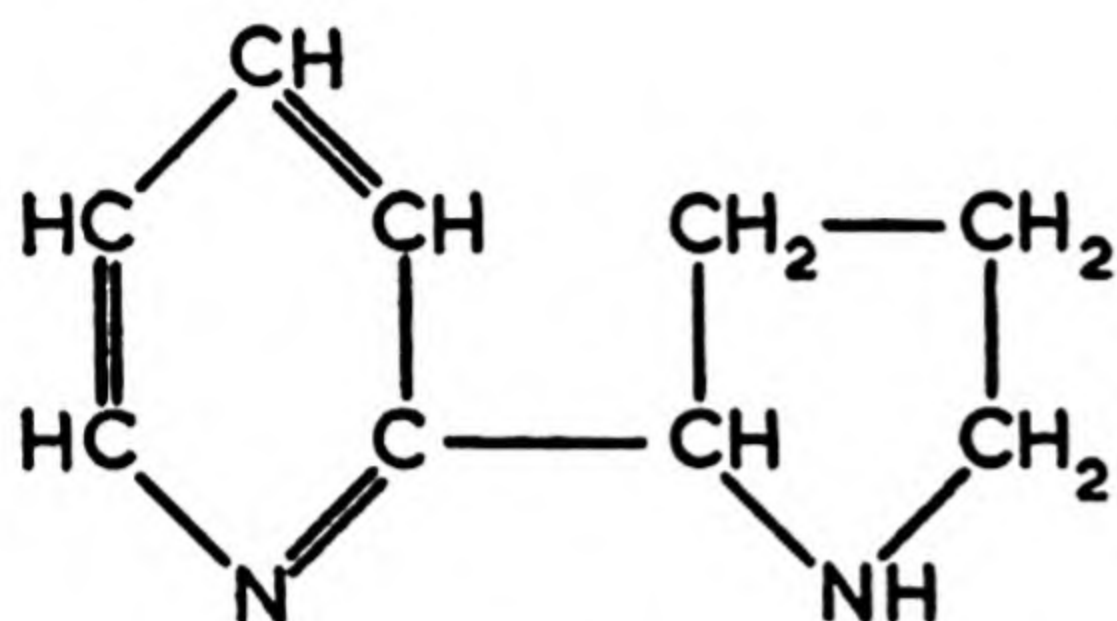
Shortly after the synthesis of neonicotine, Orechhoff and Menschikoff<sup>26</sup> isolated the same compound from the plant *Anabasis aphylla* and named the alkaloid anabasine. Smith<sup>27</sup> showed anabasine to be the optically active form of neonicotine and later<sup>28</sup> found anabasine in the roots and dried leaves of *Nicotiana glauca* to the extent of about 1 per cent. and reported that only a trace of nicotine occurred in this plant.

Anabasine is produced commercially in Russia and its use is practically confined to that country. The solution of the free base is used only to a small extent, the sulphate as a dust or spray being preferred.

Nornicotine was synthesized by Craig,<sup>29</sup> and later Smith<sup>30</sup> found that *l*-nornicotine occurred naturally in *Nicotiana sylvestris* in which it

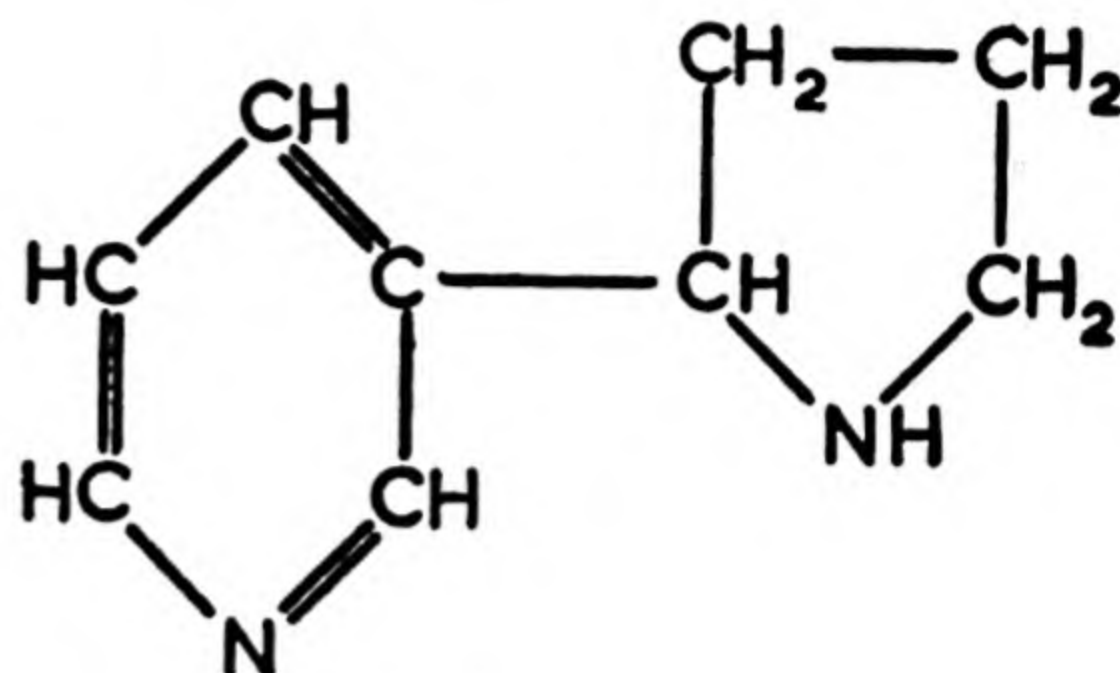


constituted 95 per cent. of the alkaloid present, the other 5 per cent. being nicotine.



$\alpha$  NORNICOTINE

Fig. 12



$\beta$  NORNICOTINE

Fig. 13

Richardson and co-workers<sup>11</sup> compared the relative toxicity of synthetic nicotines and nornicotines and summarized their results in Table 2.

TABLE 2

*Concentrations of nicotines, nornicotines and anabasines to give 50 per cent. mortality of adult wingless female bean aphid; mg. in 100 mill. of 0.25 per cent sodium oleate solution.*

Compound	Concentration
<i>l</i> -beta-Nicotine . . .	49
<i>dl</i> -beta-Nicotine . . .	96
<i>dl</i> -alpha-Nicotine . . .	1,496
<i>dl</i> -beta-Nornicotine . . .	45
<i>dl</i> -alpha-Nornicotine . . .	1,514
Anabasine . . .	5

They concluded that anabasine was considerably more toxic than the other compounds tested and that it was probably more toxic than neonicotine.



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## CHAPTER VI

### ROTENONE AND RELATED COMPOUNDS

FOR centuries it has been the practice in tropical countries to obtain fish by introducing into the water plant products which were known by experience to exert a stupefying effect. The fish which floated to the surface were then easily removed. On investigation, many of the plants used in this way proved to be members of the family *Leguminosae* and included species of derris, lonchocarpus, tephrosia, mundulea and millettia. Such plants were also used by the native population as a treatment for infestations of parasites. In fact, as early as 1848, it was suggested<sup>1</sup> that "tuba root" which was in use as a fish poison was effective against insect pests and in 1877 it was mentioned that this root was being used by the Chinese to prepare an insecticide. At the same time, it was not until after the first world war that the use of plant insecticides of this class became common.

It has been stated<sup>2</sup> that such materials began to make their appearance as a commercial insecticide on the markets of the western world between thirty and forty years ago, and that in 1911 the first application for a patent relating to derris was made. In this patent specification, there was claimed, in the manufacture of insecticides, sheep dips, animal washes, vermifuges and the like, the use of organic salt or salts, compound or compounds, obtained from the plant, bushes or trees known as "tuba robut", "tuba tedong", "acre" or "akar tuba" and "perk akal".

According to Holman,<sup>2</sup> plants of other genera have proved less effective than those of derris and lonchocarpus, and have, therefore, not become of general interest. Tattersfield and Gimingham<sup>3</sup> have reviewed the properties of many plants regarded at various times as being capable of exerting a stupefying effect upon fish. For use as an insecticide, the two species *Derris elliptica* and *Derris malacensis* are the most widely cultivated. The genus derris is found widely distributed throughout South-East Asia but the main commercial sources of derris root are the Dutch East Indies and the Malay Peninsula. The name cubé



(pronounced coobay) was employed in South America to describe species of *lonchocarpus* used for poisoning fish and it has now been adopted in commerce to describe roots of *lonchocarpus* which display insecticidal properties. Both derris and *lonchocarpus* owe their insecticidal properties to a group of compounds known as rotenoids of which the compound rotenone is the most important.

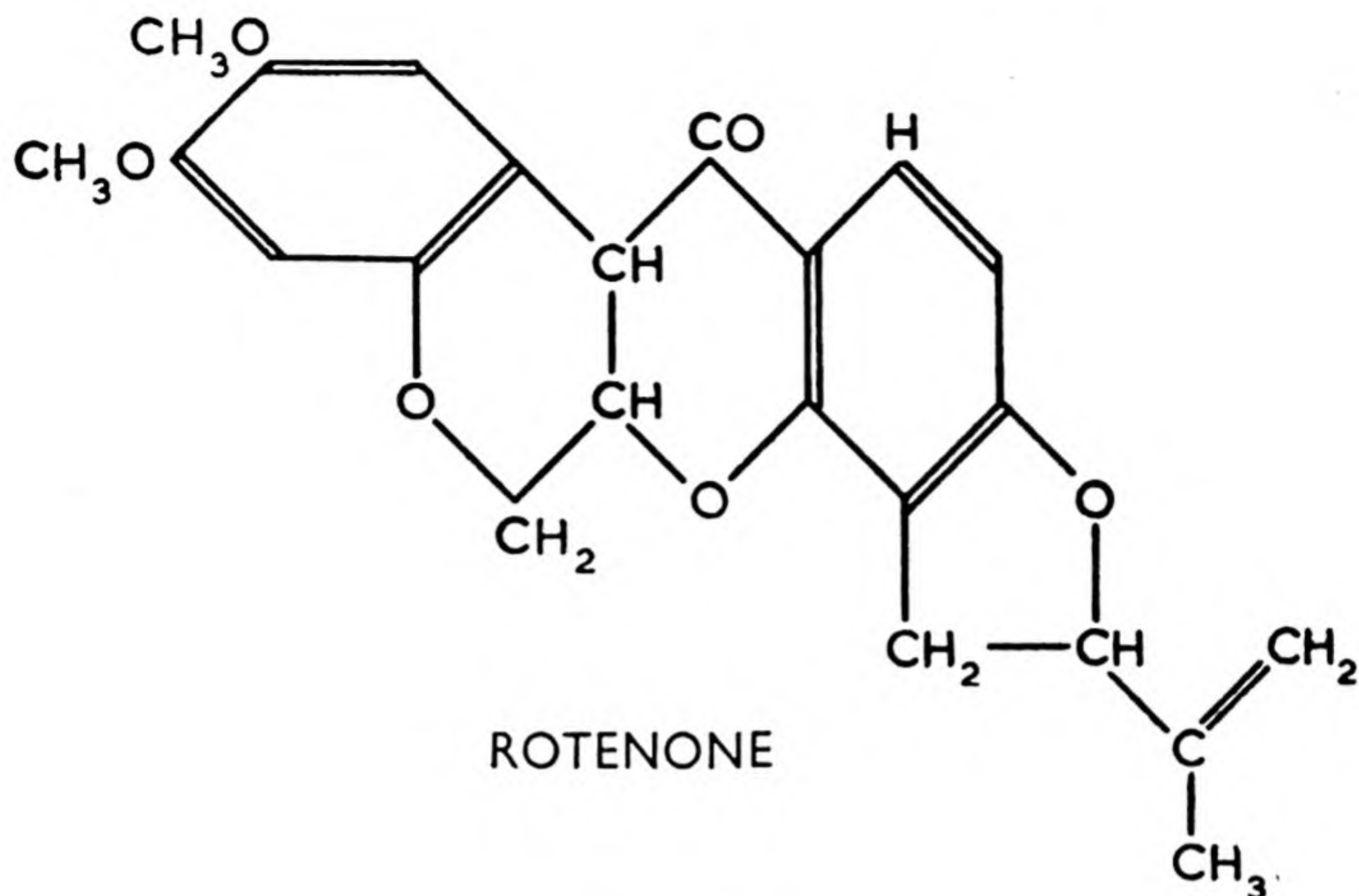
During the second world war, the loss of Malaya and the Dutch East Indies severely restricted the supply of derris and the source of rotenoids was largely restricted to the *lonchocarpus* from South America.

In 1902, Nagai<sup>4</sup> isolated rotenone from derris root and subsequently a number of workers obtained the compound and confirmed the melting point as 163° C.\* Rotenone, when pure, is a white crystalline solid and although it is soluble in the majority of organic solvents, it is practically insoluble in water. Solutions in organic solvents are optically active (laevorotatory). It is readily obtainable by extracting the root with an organic solvent such as chloroform, removing the solvent by evaporation and adding carbon tetrachloride. The rotenone forms a loose addition compound (solvate) with one molecule of carbon tetrachloride and this solvate crystallizes out. The solvate is readily broken up with alcohol to give the rotenone. This process has been used as a basis for determining the percentage of rotenone in derris root.<sup>5</sup> The elucidation of the structure of rotenone is an interesting example of the international nature of chemistry. Thus the molecular structure was advanced almost simultaneously (in 1932) by LaForge and Haller (U.S.), Robertson (Great Britain), Takei and co-workers (Japan), and by Butenandt and collaborators (Germany). This molecular formula is given in Fig. 14 overleaf.

Although Geoffrey<sup>6</sup> reported the isolation in 1892 of a crystalline compound melting point 162° C. from *Lonchocarpus nicou* and coined the name nicouline, it seems that it was not until 1923 that its identity with rotenone was established. Frear<sup>7</sup> has pointed out that although the name rotenone was adopted it would seem that nicouline should have been selected on the basis of priority.

\* In commenting on this chapter Dr. R. S. Cahn pointed out that the melting point of rotenoids depends upon the hardness of the glass tube, in very hard glass the melting point of rotenone is up to 164° C.





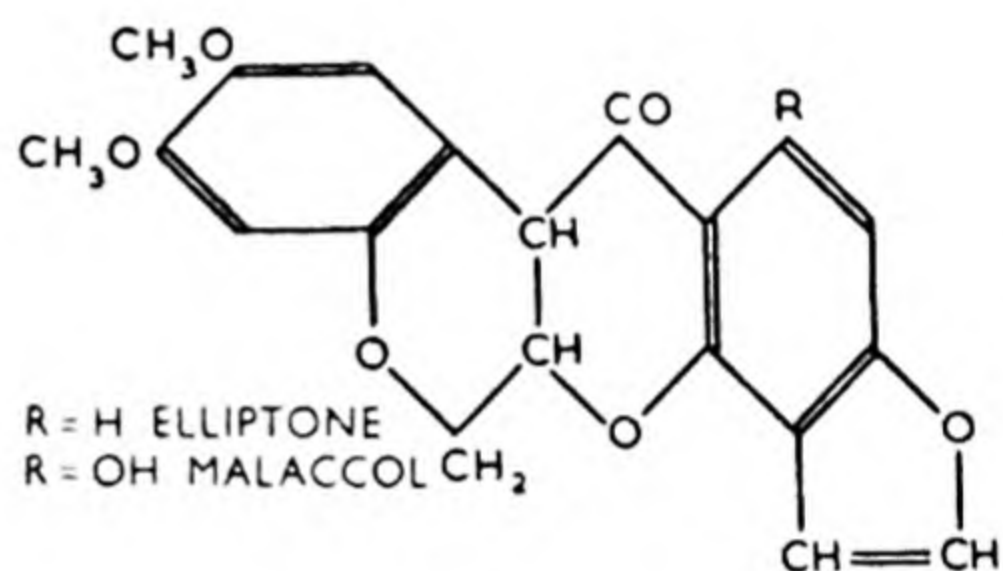
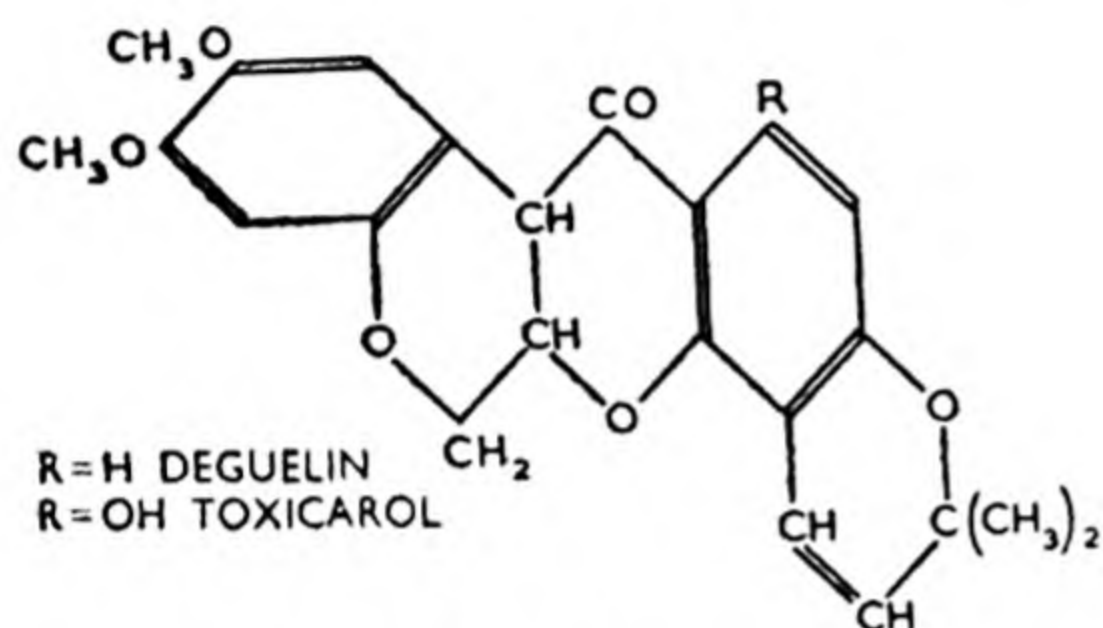
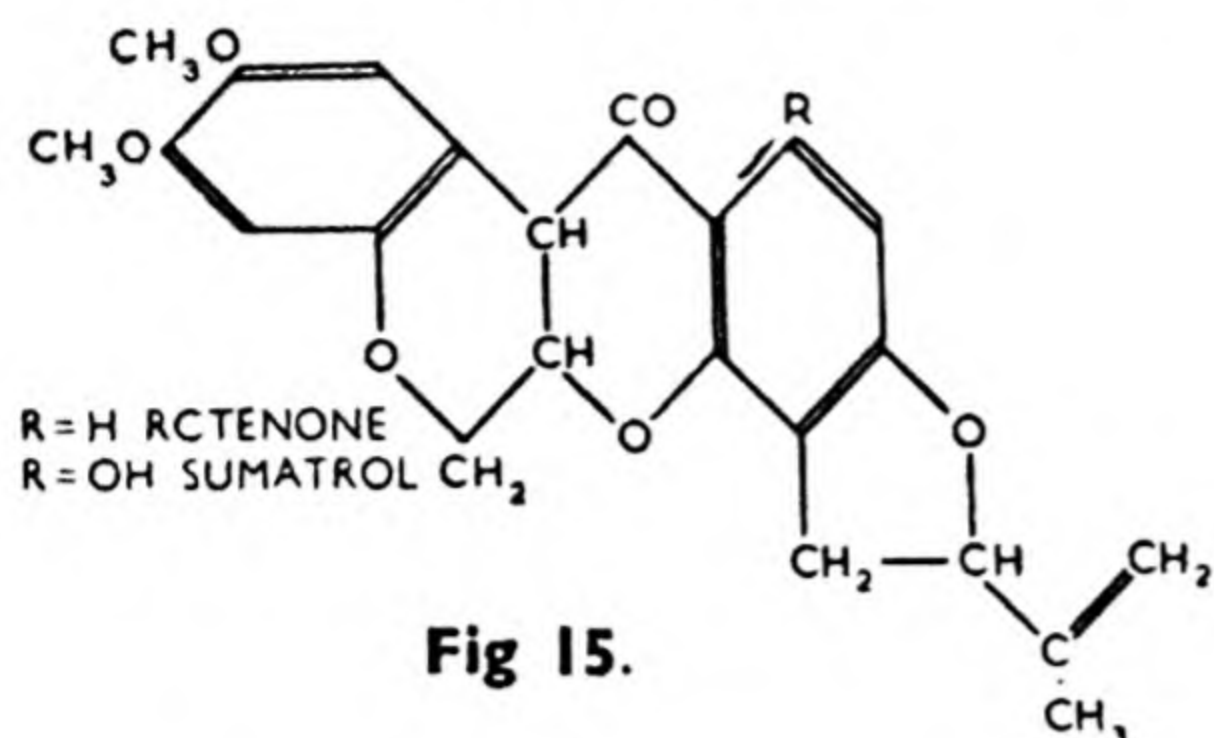
**Fig. 14**

The rotenone molecule readily absorbs two atoms of hydrogen to give a dihydroderivative and both rotenone and dihydrorotenone (claimed to be more stable in the presence of light and air) have been available commercially for some years and have been used as toxic constituents in compounded insecticides.

An excellent account of the chemistry of the rotenoids has been given recently by Harper.<sup>8</sup> Harper summarized the formulae for the chemical individuals as in Figs. 15, 16, 17.

When derris resin is extracted with an organic solvent such as ether or chloroform, the rotenone can be separated from the resin with relative ease<sup>9</sup> but the other rotenoids are only obtained from the resinous residue with difficulty. Thus it came about that originally the insecticidal action of derris and lonchocarpus was wrongly attributed solely to the rotenone content. In fact, this view received support in 1930 when Clark<sup>10</sup> treated the rotenone-free resin with alkali and separated the compounds deguelin, tephrosin and toxicarol. Each of these compounds was optically inactive as prepared by Clark and all were found to possess but little insecticidal activity.<sup>11,12</sup> The results of further





biological work showed, however, that rotenone could not be entirely responsible for the insecticidal effect and renewed efforts were made to elucidate the nature of the other constituents as they occurred in the root—or the resin prepared by simple extraction with solvents. In 1934, Haller and LaForge<sup>13</sup> prepared laevorotatory dihydrodeguelin and it was found<sup>14,15</sup> to possess considerable insecticidal activity. This work indicated that the other constituents isolated by Clark had probably been changed during the alkali treatment and Cahn and co-workers<sup>16,17</sup> submitted strong evidence to support this suggestion. Already, in 1935, Cahn and Boam<sup>18</sup> had obtained laevorotatory sumatrol subsequently shown by Robertson and co-workers<sup>19,20</sup> to be closely related to rotenone (*see* formulae). Tattersfield and Martin<sup>21</sup> then separated laevorotatory- $\alpha$ -toxicarol and Harper<sup>22</sup> confirmed their observations and extended the investigation of this constituent. Finally, two other closely related compounds, laevorotatory-elliptone and laevorotatory-malaccol, were isolated.<sup>23,24</sup>

Although, as mentioned above, Haller and LaForge isolated laevorotatory-dihydrodeguelin, the parent compound, laevorotatory-deguelin



does not yet appear to have been obtained. Harper<sup>8</sup> has pointed out that the two species *Derris elliptica* and *Derris malaccensis* are sharply differentiated by the absence in the former of *l*-sumatrol and *l*-malaccol.

Whilst it is a comparatively easy matter to determine the rotenone content<sup>5</sup> the other constituents cannot be neglected as they contribute materially to the efficacy of derris and lonchocarpus insecticides. Goodhue and Haller<sup>25</sup> devised a method of determining the deguelin content of derris and cube resins and Cahn and co-workers<sup>17</sup> utilized a method of assessing the constituents in which a phenolic group is present. Martin<sup>26</sup> separated the resin by treatment with alkali into (a) rotenone, (b) deguelin concentrate and (c) toxicarol. The relative insecticidal efficacy 1,  $\frac{1}{5}$  and  $\frac{1}{15}$  was assigned to fractions (a), (b) and (c) so that it was possible to calculate a "rotenone equivalent" for a given resin.

Recently, Jones and co-workers<sup>27</sup> compared the toxicity of derris and lonchocarpus; they considered that the toxicological value of derris and lonchocarpus of more importance than the rotenone content. Roots of *Derris elliptica*, varieties Sarawak creeping and Changi No. 3 (low rotenone and high rotenone), *Lonchocarpus utilis* and *Lonchocarpus chrysophyllus* were extracted with acetone and the dried extract dissolved in acetone to give solutions with a standard rotenone content. The solutions were tested biologically against adult house-flies and examined chemically to confirm the proportions of rotenone and rotenoids.

The derris samples were found to be relatively more toxic than the lonchocarpus. Jones and co-workers concluded that, assuming that their samples were more or less representative of the species and varieties examined, the toxicity to house-flies was a fair measure of the toxicological value of the samples. It would appear, other factors being equal, that the Sarawak creeping or the high rotenone Changi No. 3 varieties of derris are the best varieties for producing insecticidal material. The colorimetric determinations\* of the rotenone equivalent varied from 14 per cent. below to 38 per cent. above the toxicological rotenone equivalent.

\* Colorimetric determination, analysis based on the colour of solutions being proportional to the amount of substance in solution.



Wilson and Jackson<sup>28</sup> observed that the particle size of diluents used with rotenone dusts had an important bearing on the efficiency of the dusts. When the particle size was too large (60 mesh) the dusts were less effective than when the size was of the order 200 to 325 mesh. A very small particle size (1 to 10 microns) greatly reduced the efficiency of rotenone dusts, the colloidal particles tend to cover the particles of the derris and cube and thereby prevent their coming into contact with the insect. The chief source of such colloidal particles are free ferrous and ferric oxide and chloritoid minerals.

It has been shown<sup>2</sup> that derris and allied materials are comparatively safe to man and higher animals but workers handling derris dusts should wear a respirator to prevent the ingestion of the dust.

Tischler<sup>29</sup> has reported that derris extracts enter the insect's alimentary canal through the spiracles and through the integument, derris dusts exert their toxicity by entering the alimentary canal and through the integument. Derris inhibits utilization of oxygen in the insect and this effect is general rather than specific to any organ or system.<sup>2</sup>

Cahn and co-workers<sup>30</sup> have reported researches on the stability of derris in insecticidal dusts which led to the development of the anti-louse powder 63 (A.L. 63). In this dust the immediate lethal effect was due to finely divided naphthalene and the protective effect, lasting for five to eight days, was due to ground derris root or cube extract admixed with a small amount of high boiling tar acid.

The use of rotenone as a plant protective has largely been concerned with the necessity of finding an insecticide which is harmless to man and can therefore be applied to vegetable and fruit late in the season immediately before lifting or picking of the crop. For late season application, insecticides such as lead arsenate leave undesirable residues and in many countries their use at this time is forbidden by legislation; in such cases, rotenone compounds are usually applied.

A large proportion of the rotenone preparations are used as substitutes for arsenicals on brassica crops where they are usually applied as dusts, containing the ground root and an inert carrier. The total active ingredients generally approximate to 2.5–5 per cent. and the carrier is often talc.

For application to horticultural crops, the question of undesirable



residues is of paramount importance and rotenone or derris preparations have been used to a considerable extent. While ground root preparations can be used, it has been found that a more satisfactory dispersion of the active materials can be obtained by using an extract of the root resins in which the solvent is, to some extent, miscible with the water used as a diluent. The "colloidal" suspension so formed, when used in conjunction with a suitable wetter, is effective as a controlling agent against caterpillars, sawfly larvae, red spider, thrips and aphids. Its effect appears to be more pronounced when it is used with an oil emulsion in which case the resin particles collect at the water-oil interface and are left on the plant surface with the oil deposit left by the disruption of the emulsion into its component phases.

Farmers in this country are required, by the warble-fly order of 1936, to use a derris insecticide for the control of warble-fly larvae in cattle.

A number of reviews<sup>2, 31, 32, 33, 34</sup> of the literature and uses of rotenone-containing substances have been published.

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## CHAPTER VII

### ARSENICAL COMPOUNDS

ARSENICAL compounds are numbered amongst the earliest human poisons to man and their possibilities as insecticides appreciated as long ago as 1681<sup>1</sup> when John Worlidge in his *Systema Agriculturae; the Mystery of Husbandry Discovered* referred to their use for the control of ants in the following words: "Also you may make Boxes of Cards or Pasteboard pierced full of holes with a Bodkin, into which Boxes put the powder of Arsenick mingled with a little Honey; hang these Boxes on the Tree, and they will certainly destroy them (the ants); make not the holes so large that a Bee may enter, lest it destroy them." This method, with slight modifications, is still in use to-day. Although there are other early references to the use of arsenic compounds, for instance to control lice and ticks, the real history of these materials commenced in the middle nineteenth century and their success can be gauged by the fact that they are the most widely used of all stomach poisons.

The basic material from which the arsenic group of insecticides are prepared is white arsenic ( $\text{As}_2\text{O}_3$ ) recovered by sublimation from the flue dust of smelting factories using arsenic-containing ores. It has been estimated<sup>2</sup> that during 1941, in the United States alone, approximately 31,000 short tons of white arsenic were converted into some 157,000,000 tons of arsenical insecticides among which were the arsenates of calcium and lead, Paris green, London purple and sodium arsenite.

The arsenical insecticides are stomach poisons and are applied as a protective covering over the plant surface by dusting or by spraying. **Paris Green** is a copper aceto-arsenite  $(\text{CH}_3\text{COO})_2\text{Cu} \cdot 3\text{Cu}(\text{AsO}_2)_2$ , and when pure contains 58.55 per cent. of arsenious oxide; the commercial preparations, however, vary in the content of arsenious oxide and an average taken of 499 samples<sup>3</sup> gave only 56.56 per cent. content. Paris green was first prepared in 1814 and was then used commercially as a pigment.

Paris green was declining in popularity as a colouring matter when, in 1867–1870,<sup>4</sup> it was tried as a dust against the newly invading Colorado



beetle in the potato fields of eastern United States. Its success established it as the standard insecticide and it was accordingly tried against the canker worm (*Alsophila pometaria*)<sup>5</sup> and the codling moth.<sup>6</sup> While its capabilities as an insecticide were clearly demonstrated, it suffered the disadvantage of being phytotoxic and was liable to cause severe foliage damage.

In the early stages of its use as an insecticide, it was found to vary considerably in its composition, but methods of manufacture were later standardized to give a product of more uniform consistency. Nevertheless, it was rapidly replaced as a horticultural insecticide, chiefly because it breaks down in water to release soluble phytotoxic arsenic compounds with resultant foliage burn, and partly because of its poor suspension and adhesive properties. It is still used on a very considerable scale in the United States for the control of cotton pests.

Paris green has found a wide application as a larvicide for the control of mosquito larvae. It is blown over the surface of the water as a finely divided dust which floats on the surface and is ingested by larvae. Used for this purpose, it has been employed as a dust from aeroplanes, but considerable attention must be paid to the particle size; thus Metcalfe and Hess<sup>7</sup> have reported that if the average particle size is less than 20 microns, the dust drifts away from its objective while, on the other hand, if the powder is too coarse, the mosquito larvae are unable to ingest them. Paris green is also used as a poison for baits to control various pests such as leatherjackets in the garden, but for wide-scale operations, it is more usual to employ sodium arsenite.

Roark<sup>8</sup> has reviewed a number of experiments with arsenical compounds possessing a structure similar to Paris green in which the acetic acid radicle has been replaced by various organic acids or mixed acids obtained by the saponification of vegetable or animal oils. Although these compounds have been tested only to a limited extent, Roark considers them worthy of attention; Table 3 summarizes the results obtained when using similar concentrations of each compound against the Japanese beetle, *Popillia japonica*.

As further tests against other insects also showed that some of these compounds possessed considerable toxicity, Roark suggested some possible uses for them in which advantage could be taken of their other



TABLE 3

Material	Coefficient of effectiveness	Foliage injury
Lead arsenate . . . . .	1.00	Slight
Copper crotonoarsenite . . . . .	.73	Moderate
Paris green . . . . .	.68	Slight
Copper palmitoarsenite . . . . .	.64	Slight
Paris green and flour . . . . .	.60	Moderate
Tung-oil green . . . . .	.56	Slight
Cotton seed-oil green . . . . .	.55	Moderate
Paris green and summer oil . . . . .	.54	Slight
Copper lauroarsenite . . . . .	.38	Severe
Soybean-oil green . . . . .	.28	Slight
Copper stearoarsenite . . . . .	.24	Very Slight
Copper oleoarsenite . . . . .	.24	Slight
Rape seed-oil green . . . . .	.09	Moderate

properties; thus the formic acid green has a high arsenic content and might give a more rapid kill than Paris green, while the oleic and stearic acid greens might be non-phytoxic as they release little soluble arsenic when added to water; the two latter compounds are also oil-soluble and could thus be easily incorporated into horticultural oil sprays while their considerable copper content might convey some fungicidal action. In spite of these suggestions, there has been no further work to indicate that these materials can be used as economic insecticides with a greater efficiency than lead arsenate.

The deleterious effects of Paris green on foliage led to a search for other arsenical compounds which would be safer in use. The most useful of these was **Lead Arsenate** which was prepared by Moulton in 1892 by reacting lead acetate with disodium arsenate. The first trials were against the gypsy moth (*Lymantria dispar*) and from that time it has shown such consistent results with the minimum of plant damage



that it has become the leading protective stomach insecticide in all areas of the world.<sup>3</sup>



Fig. 18.—Codling moth larva on a section of apple. *A Shell Photograph.*

Lead arsenate exists as a number of salts but it is the acid lead arsenate,  $\text{PbHAsO}_4$ , which is in general use as an insecticide. This form is almost insoluble in water and thus relatively free from phytotoxic effects; in spite of the presence of the heavy lead atom, it suspends fairly easily in water and can be used either as a dust or spray whilst it is compatible with a number of other important plant protectives such as lime sulphur and petroleum oil sprays.

Lead arsenate is now used as a universal stomach poison against chewing insects on fruit trees, vegetables and fodder crops; the greatest offtake, however, is for the control of codling moth on apples.

Spray injury may result from the use of lead arsenate if the water is



hard and rich in bicarbonate which react to form soluble arsenical compounds. In an investigation into this aspect, Ginsburg<sup>9</sup> concluded that while soaps will restrict plant injury in these cases, they cannot be recommended for general use as they have the opposite effect in soft waters. The same author<sup>10</sup> has also investigated the effect of "correctives", which are subsidiary chemicals added to minimize plant injury effects, but when lead arsenate is used alone it is not the general practice to use such materials as the incidence of damage is relatively low. Wetting and spreading agents and stickers are frequently included in a lead arsenate spray to enhance the evenness and tenacity of the deposit.

Lead arsenate is often used with lime sulphur to form a combination spray for the control of foliage caterpillars and scab (*Venturia inaequalis*) on apples. The two materials may react with the formation of phytotoxic soluble arsenical compounds, especially if there is a long delay between mixing and application; Goodwin and Martin<sup>11</sup> have studied the complex reactions which take place and concluded that the formation of the soluble arsenic is accelerated when the lead arsenate is finely divided and thus offers a maximum surface area to reaction. The phytotoxic effects of this combination spray may be minimized by using grades of lead arsenate which are coarser than 300-mesh particle size and by the addition of certain "safeners" or "correctives" which hinder the reaction between the two chemicals. Kearns *et al.*<sup>12</sup> have successfully demonstrated that ferrous sulphate can be used as a "safener" and possesses the additional advantage of also reducing lime-sulphur damage; within the last few years, manganese sulphate<sup>13</sup> has also been used for the same purpose.

Although **Calcium arsenate** was used as an insecticide prior to 1911, its status as a popular insecticide was brought about in the first world war when the price of lead rose sufficiently to make lead arsenate an expensive plant protective. Since that time, it has held its place, particularly for use against cotton pests, and in the United States the total consumption is now greater than that of lead arsenate.<sup>2</sup>

Calcium arsenate also exists in a number of salts of which the dicalcium arsenate,  $\text{CaHAsO}_4$ , is the one used as a plant protective. According to Martin,<sup>14</sup> commercial calcium arsenates are prepared so as to contain an excess of lime as the dicalcium salt alone is too soluble



for safe application to foliage. Calcium arsenate is used principally against the cotton boll weevil, but has found other applications such as dusting from aeroplanes for the control of forest pests, for example, the gipsy moth in pine forests, and also for the treatment of vines to control the grape berry moth where both lead arsenate and barium fluosilicate may leave undesirable residues in the wine. In general, however, except where foliage damage is of only secondary importance, lead arsenate has a more universal application than the calcium salt.

Other arsenical preparations have specialized uses; thus sodium arsenite has had wide application in the use of poison baits for the control of cutworms, mole crickets and particularly locusts and grasshoppers. Locust bait consists of 2 per cent. sodium arsenite in bran moistened with an equal weight of water, and is cast thinly among the feeding locust hoppers; although the main attractant in the bait is the moisture, the bran itself also exerts an attraction as similar baits made with sawdust are not so effective. Sodium arsenite will also kill insects when applied as a dust, but it is doubtful whether it is acting as a contact insecticide or whether it is conveyed to the mouth when the insect endeavours to free its antennae and legs from the dust; on the other hand, 2 per cent. solutions of sodium arsenite in water will kill locusts if sprayed on them and here there seems to be true contact action.

Manganese arsenate, which is brown in colour, has found a use for the control of pests attacking ornamental shrubs where the characteristic white deposit left by most arsenical compounds would be unsightly; similarly, it has been used on cured tobacco to avoid the appearance of mould caused by other arsenical preparations.<sup>3</sup> Many arsenical preparations are the basis of sheep and cattle dips used for the control of sheep scab, lice, ticks and keds; in an investigation into the toxic effects of various arsenical compounds to animal pests, Freney and co-workers<sup>3</sup> concluded that sodium arsenite was the most effective and that whilst trivalent and pentavalent arsenicals will both kill adult lice, the trivalent compounds are the more efficient for the control of ked.

Care must be exercised in the amount of arsenical residues remaining on the fruit or plant at the time of picking or harvesting. Most countries have adopted legislation on this point, and it is often necessary for the farmer to strike a careful balance between full insect control and the



possible condemnation of his crop for consumption. With certain hard fruits, the residue may be removed mechanically with hand wiping or with washing apparatus, but the most effective methods entail washing in dilute solutions of hydrochloric acid. These methods cannot be used on soft fruits such as grapes, and it is therefore not possible to employ arsenical compounds or other stomach poisons for some weeks prior to harvest.

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## CHAPTER VIII

### PETROLEUM OILS \*

THE insecticidal powers of crude petroleum were well known to the ancients, and it is interesting to note that even to-day, the Bedou of Central Arabia welcome from the occasional traveller a gift of petrol which they liberally sponge on their camels and themselves as a universal panacea for parasites. The relatively modern use of petroleum oils would appear to date from the middle nineteenth century when the losses caused by citrus scale insects in America turned attention to the use of kerosene as a scalcicide; although the pest control was partially satisfactory, the damage occasioned to the trees by undiluted kerosene led to a search for a kerosene-water emulsion by which the amount of oil employed would be reduced while at the same time preserving an even and continuous coverage. Various emulsions were tried, using milk or soap as emulsifiers until in 1880, the formula of Riley and Hubbard<sup>1</sup> gained a popularity which lasted for some years.

The kerosene emulsions, although an improvement on the undiluted oil, still occasioned plant damage and as this was attributed to volatility, the use of crude petroleum and lubricating oil emulsions was tried, but with such indifferent success that they were unable to compete with lime sulphur as a scalcicide. It was not until the years following 1922 that improvements in base oil refining and a better understanding of the formulation of stable emulsions enabled petroleum oils to regain their place as plant protectives, and since the introduction of Volck's emulsion concentrate, which did much to popularize this form of pest control, the use of petroleum oils in one form or another has become almost universal.

#### The base oils for horticultural sprays

Crude petroleum oils are subject to distillation yielding a range of fractions according to their boiling range and viscosity. It is the middle

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of this range comprising the kerosenes, gas oils and lubricating oils which are generally used for insecticidal purposes, the more volatile kerosene group being used as solvents for fly and mosquito sprays, and the lubricating group as base oils for horticultural washes.

The process of distillation separates the fractions largely according to molecular weight and viscosity, and it is possible to make an approximate classification based on the hydrocarbons contained in them, *e.g.* kerosenes contained hydrocarbon molecules of 10–16 atoms and lubrication oils 14–18 carbon atoms. This classification takes no note of chemical composition, for oils are composed of a wide variety of hydrocarbons falling into the following four groups :

1. Saturated hydrocarbons—paraffins
2. Olefine series of unsaturated hydrocarbons
3. Aromatic ring hydrocarbons, and
4. Complete or partially hydrogenated ring compounds—the naphthenes.

The proportion of the various hydrocarbon groups and also the amount of impurities such as sulphur compounds and nitrogenous derivatives vary according to the origin of the oil and two fractions of the same boiling range, but from different crudes, may be chemically very different in composition. It is usual, therefore, to classify the crude oils as paraffinic or naphthenic according to the preponderance of these compounds left in the residue after distillation, and at the same time to specify the place of origin, *e.g.* Pennsylvania or Venezuela.

The oil fractions are refined either by solvent processes or by treatment with sulphuric acid or sulphur dioxide which removes all but the saturated hydrocarbons proportionally to the degree of refinement. At the same time these processes, which involve treatment with cleaning earths, remove the colour of the oil so that it is possible to classify the degree of refinement visually, thus highly refined oil is spoken of as “white oil” while next in degree is “half white” and the last refined the “red”. These terms must be used with some degree of caution, as in some parts of Europe it is customary to refer to any petroleum horticultural wash as a “white oil spray” irrespective of the degree of



refinement of the base oil. The fundamental reactions of animal and plant tissues to oil are still obscure, and the specifications of insecticidal oils have, up to the present, been largely empirical. The basis of the classification of spray oils rests on certain chemical and physical characters which are as follows:

**The unsulphonated residue** which is an index of the degree of refinement of the oil and is determined chemically by reacting a known volume of the oil with concentrated sulphuric acid, and observing the percentage which is not absorbed by the acid. In this process, the saturated hydrocarbons remain unattacked, but the other groups are sulphonated or polymerized into an acid sludge. As the saturated hydrocarbons are less toxic to plants this test indicates the degree of "safety" of the oil for horticultural application, and the U.M.R. (unsulphonated mineral residue, after sulphuric acid treatment in standard conditions) is one of the more important properties distinguishing winter washes (U.M.R. 65 per cent.–80 per cent. approx.) applied to the resistant dormant plant, from the summer sprays (U.M.R. above 90 per cent.) for use in the more delicate full foliage stage. It should be noted that this test, which is the usual one employed, does not give a direct value for the aromatic hydrocarbons as these together with the other unsaturates are removed by the acids. A more accurate determination of the factors generally believed to be concerned with phytotoxicity can be made by reacting the oil with iodine which, combining with the unsaturates at the points of double bonded carbon atoms, gives a relative value of the total number of unsaturated bonds in the mixture of hydrocarbons composing the oil.

**Viscosity and boiling range**, both of which increase as a homologous series of hydrocarbons is ascended. As oils are a mixture of hydrocarbons, these physical characters are associated with the mean molecular weight of the mixture, and do not indicate the proportions of the component groups. Viscosity is measured by the rate of the flow of a given volume of oil, through an orifice of standard dimensions at a specified temperature; the viscometers used for this purpose not only vary in world areas, but the specified test temperatures are also different and results obtained can only be correlated by means of tables. The systems in use are:



	Viscometer	Usual viscosity temperatures
British Empire .	Redwood	70° F. 140° F. 200° F.
America . . .	Saybolt	100° F. 130° F. 210° F.
Europe . . .	Engler	20° C. 50° C. 100° C.

A more accurate determination of viscosity can be made by measuring the force needed to shear an oil film of given thickness at unit speed and expressing the results in centimetre-gram-second units termed "stokes" and "centistokes". This method is not in general usage for viscosity definitions in relation to base oils for horticultural use and the viscometer methods described above serve to give values which are approximately proportional to the true viscosity.

**Volatility** which is of importance as the permanence of an oil film may have direct bearing on the mortality of some insects and may also be concerned with plant damage. Volatility is measured by the loss in weight of a given quantity of oil from a standard container at a controlled temperature, but it is more usual and convenient to assess volatility for horticultural base oil by the percentage of neutral oil which distils over at a fixed temperature in standard conditions. Oils of different origin exhibit different volatility and whereas refining processes will change the viscosity of a fraction, the volatility remains the same.

**Specific gravity**, which is correlated with boiling range, but is also affected by the proportions of the different series of hydrocarbons and may therefore be altered by simple blending.

The official specifications for petroleum sprays are based on the characteristics described above. There is, however, a growing feeling that these standards are not sufficient and that with further knowledge of the reaction of insect and plant tissue to oil, other characters of the base oil will be included in the specifications.

### **Insecticidal action of petroleum oils**

While petroleum oil is undoubtedly lethal to the majority of insects if brought into intimate contact with them, the mode of action is still



controversial. Among the well-known theories that have been advanced, two have deserved most attention; these are:

1. That the oil invests the insect and acts as a mechanical barrier isolating it from atmospheric oxygen and so stifling it, and
2. That the components of the oil or its derivatives act with direct toxicity on the insect tissues. It seems probable that both these explanations are valid in varying circumstances.

Oil can readily enter the insect trachea, partly perhaps by capillarity, but probably also by the respiratory movements of the muscles coupled with the apparent affinity of the oil for the tracheal lining. As the oil advances deeper into the trachea and tracheoles, the pressure drives the imprisoned air into solution in the body tissues until no gaseous oxygen is present<sup>2</sup>; this not only leads to disruption of the respiratory system, but at the same time, the oil is in intimate contact with the insect interior and is well placed for any toxic action. As an ovicide an oil film enveloping the egg may well stifle the embryo, providing that the film persists for a long enough period,<sup>3</sup> but it has also been shown that actual penetration to the embryo occurs with some insect eggs<sup>4</sup> when presumably a toxic action is produced before any stifling effect can take place. Some insects, *e.g.* the overwintering eggs of *Aphididae* and *Psyllidae*, are resistant to petroleum oil, but succumb to tar oils (carbolineums) due to the presence of certain hydrocarbons present in the latter but absent in the petroleum. Where persistence of the oil film is an important factor, the higher the viscosity the more effective the oil. With adult and larval insects where entrance into the body is probably necessary, penetration into the tracheae is facilitated by oils of low viscosity, though not proportionately, except within a homologous series\* of related oils.<sup>5</sup>

The qualities of oil which render it toxic to insects are still obscure. By analogy with phytotoxicity it has in many cases been assumed that the unsaturated hydrocarbons in the oil are responsible for the lethal effect, but the evidence on this point is very conflicting. De Ong<sup>6</sup> investigating the control of scale insects concluded that the sulphon-

\* Homologous series, a series of related organic compounds of increasing molecular weight.



atable portion of the oil was related to insect kill but Cressman and Dawsey<sup>7</sup> and others<sup>8,9</sup> were unable to confirm this. Ebeling,<sup>10</sup> using the potato tuber moth (*Gnorimoschema operculella*) as a test insect, found no relation between kill and viscosity or distillation range of regular citrus oils, but that the more volatile kerosene was more toxic. He furthermore found no difference between the toxicity of naphthenic or paraffinic oils and that with both, the kill increased with the sulphonatable proportion of the oil. He has suggested that where experiments have shown no difference in toxicity with varying proportions of unsaturates, the test insects used were of such a nature that they die of suffocation before any toxic reaction can take place. On the other hand, Pearce *et al.*<sup>11</sup> examining dormant type oils showed that the minimum effective dosage is closely related to physical characters such as viscosity, density, refractive index and aniline point which are all indicative of the structural constitution of the oil, *i.e.* paraffinic or naphthenic; they conclude there is a high correlation between efficiency and paraffinity, and that the aromatic ring content acts merely as a diluent with no lethal effect. Similar work by Chapman *et al.*<sup>12</sup> on base oils for summer sprays led to the same conclusions. The apparent incompatibility of the conclusions found by different workers may well be the result of using test insects which react differently to petroleum oils, and it would appear essential that experimental work should be carried out on those pests which are of economic importance in the field if the farmer is to benefit by such research.

The works to which reference has been made above are concerned chiefly with the base oils of horticultural sprays which are generally fractions within the lubricating oil range. With the more volatile fractions in the kerosene range, toxic action alone can be responsible for insect kill as the resultant film is not persistent enough to cause suffocation. Shafer<sup>1</sup> has shown that vapours from kerosene have an anaesthetic effect on insects but they can expel these on removal to pure air and often recover; Moore *et al.*<sup>13</sup> found that the volatile fractions will kill houseflies but an exposure of 400 minutes is necessary to accomplish this. Kerosene is also more lethal than the lubricating oils when used as a contact insecticide by placing a drop on a particular spot of the insect cuticle, but its toxicity is not sufficient for it to be used alone as a



fly spray and it is customary for such preparations to be formulated with refined kerosene acting as a carrier for a knockdown agent such as pyrethrum extract and a lethal agent such as D.D.T.

The limiting factor in the employment of petroleum oils is, in the first place, their phytotoxicity; thus while base oils containing at least 60 per cent. of unsulphonated residue have been used for plants in the dormant stage, of necessity the more highly refined oils containing 90–96 per cent. U.M.R. must be used for summer plants in full foliage. Only after fulfilling these basic limitations is it possible to consider the practical aspect of toxicity to insects.

### Petroleum oils and phytotoxicity

The killing of many of our insect pests by petroleum washes would be relatively simple were it not for the phytotoxic effect of oil which often proves to be the limiting factor. To ensure control of a pest without incurring plant damage, it is necessary to strike a careful balance of several factors which fall broadly into two classes, but which are, themselves, interdependent. These classes are:

1. The physical and chemical nature of the oil; and
2. The amount of film deposit retained on the plant surface.

Injury by oil to plants may be either acute or chronic. Acute injury is readily perceptible within a matter of days after application and is marked by foliage burn followed later by leaf drop, but seldom with injury to the wood and fruit. Chronic injury, on the other hand, may persist and develop for long periods after application and is shown by bud kill and delayed bud development, yellowing of leaves, and death of the wood.<sup>14</sup> With both types of injury the quality of the oil is of prime importance.

De Ong and Gray<sup>15</sup> came to the conclusion, since substantiated by Kearns *et al.*<sup>16</sup> and many other workers that the unsaturated hydrocarbons, which are capable of being removed by sulphuric acid treatment, are to a large extent bound up with plant damage. Although this has proved a most valuable contribution and enabled Martin<sup>17</sup> to make recommendations upon which the United Kingdom specification for winter washes and summer spray oils is based, there is nevertheless, no



exact correlation between the sulphonatable proportion and the amount of damage. It has been suggested that not all the unsaturates are removed by sulphuric acid and that these remain in the refined oil causing varying degrees of damage.<sup>1</sup> It has further been shown<sup>18</sup> that some of the oxidation products of petroleum are acidic and polar and that these probably pass more readily through cell walls than the unoxidized compounds.

After application, the oil film disappears from the leaf surface with a greater rapidity than would be accounted for by volatilization and adsorption by the plant seems mainly to be responsible. Penetration by oil into the tissues causes disturbances to photosynthesis, transpiration and respiration<sup>19,20</sup> and with heavy applications it may penetrate considerable distances<sup>21</sup> but Rohrbaugh<sup>1</sup> considers that with normal spray dosages the oil largely remains just under the epidermis of leaves, twigs and fruit, and that much of it is lost when normal leaf shed occurs. Ginsburg<sup>22</sup> found that penetration appears to vary indirectly with the viscosity but, in general, experimental work has shown that with saturated hydrocarbons of low viscosity, a greater degree of safety is obtained than with high viscosity saturates. Pearce *et al.*<sup>11</sup> when investigating the insecticidal action of paraffinic and naphthenic base oils state that there is an indication that paraffinic oils are not only safer to use from the phytotoxic aspect, but also that their greater efficiency as insecticides will permit their use in less quantity which will also lessen the risk of plant damage.

The present position can be fairly summed up by stating that although it has been possible to lay down certain practical standards for the base oils of horticultural sprays, these are essentially empirical and we are still a long way from a complete understanding of the toxic action on plants. With greater knowledge of the chemistry of the various hydrocarbon components of oil and their mode of interference with the physiology of plants, it can be expected that a revision of the specifications for these oils will be made.

With the conventional spray machines now in use, oils suitable for insect control cannot be applied directly to plant tissues without giving a deposit which is heavy enough to cause damage. It is therefore necessary to apply the oil dispersed in water as an emulsion in order to



reduce the oil deposit below that which will cause damage. A suitably formulated emulsion remains stable in the tank of the spray machine but on impact with the plant surface it breaks up into the component phases leaving a uniform continuous oil film while the surplus water phase evaporates or runs off together with the surplus emulsion.

The heaviness of the oil deposit depends not only on the oil concentration but also on the emulsifier used. A very stable emulsion which does not readily separate into the oil and water phases leaves only a light deposit for much of the oil runs off as unbroken emulsion; a quick-breaking emulsion, on the other hand, will leave a maximum deposit.<sup>14</sup> The choice of an emulsifier is therefore one of prime consideration and is used to regulate the oil deposit for a particular type of spray to secure the maximum of insecticidal activity consonant with safety in respect of the plant tissue.

### **Practical aspects of petroleum sprays**

Petroleum sprays can be formulated in a number of ways which, however, fall broadly into two classes. The first of these is the concentrated emulsion or mayonnaise in which a large volume of oil is already dispersed in a comparatively small volume of water by the aid of an emulsifier. For field use, this concentrate is simply diluted with water until the ready-to-use spray contains the desired percentage of oil. These mayonnaise type concentrates have the great advantage that they can be formulated to make stable dilute emulsions in hard water; on the other hand, they are susceptible to deterioration in storage. The viscosity of the concentrate, an important aspect in convenience of handling, can to a wide extent be controlled by the method of manufacture as this depends on variation in the sizes of the oil droplets in the dispersing water phase.

The second type of spray oil concentrates are known as "miscible oils", "soluble oils" or "emulsible oils". They contain very little or no water, but have dissolved in them an oil soluble emulsifier so that immediate emulsification takes place when diluting with water for field use. They can be manufactured to give any degree of stability, oil deposit and speed of breaking on impact by varying the amount and kind of emulsifier. They possess the advantage of being easy to handle



and to suffer no deterioration during storage, but while formulations based on soaps are not so tolerant to hard water, this disability is completely overcome by developments in the use of non-ionic emulsifiers.

Horticultural sprays can also be classified according to their use as winter washes or summer sprays. Winter washes, whose base oil generally has a value of 65–80 per cent. U.M.R., are applied to deciduous trees in the dormant stage, or with slightly more risk but often with increased insecticidal action in the “delayed dormant” stage between bud burst and the unfolding of the first foliage. Their purpose is to kill the overwintering eggs of *Capsidae* and *Acarini* (e.g. red spider). Although petroleum washes alone are unable to control the overwintering eggs of *Aphididae* and *Psyllidae*, the incorporation of dinitro-*ortho*-cresol enables them to fulfil this function<sup>23,24</sup> thus conferring on a single petroleum wash all the advantages which formerly necessitated a dual treatment of tar oil spray followed by petroleum wash.

Winter washes at the present time are used either alone or in one or two combinations of which that with dinitro-*ortho*-cresol is the most common. Recently, it has been shown that the incorporation of D.D.T. enables the spray not only to control the usual winter complex of pests, but also apple blossom weevil, for which it has formerly been necessary to apply a separate treatment.

The use of summer petroleum sprays is much more diverse for these highly refined oils of U.M.R. greater than 90 per cent. not only possess a toxicity themselves against many pests but they also have the additional advantage of being excellent media for the carrying of other insecticides and fungicides. In the tropics and sub-tropics, summer petroleum washes are used on a very wide scale to control scale insects of fruits, notably citrus, and a fungicide of the Bordeaux Mixture type is often added to control fungi. In the more temperate zones on deciduous trees in full foliage and on glasshouse plants, much use is made of combined sprays, the additions being as diverse as nicotine, rotenone compounds, D.D.T., lead arsenate and copper fungicides. While the summer sprays alone give excellent control of the acarines and scale pests, the advantages of a combined spray are multiple; firstly, it may be directed against a single pest and the insecticidal power



of the reinforced spray by the additive, *e.g.* the incorporation of rotenone compounds for the control of severe attacks of red spider; secondly, the spray may be directed against a range of pests, for example, using combined petroleum spray and fungicide for the control of red spider and *Cladosporium* on tomatoes. Furthermore, the oil

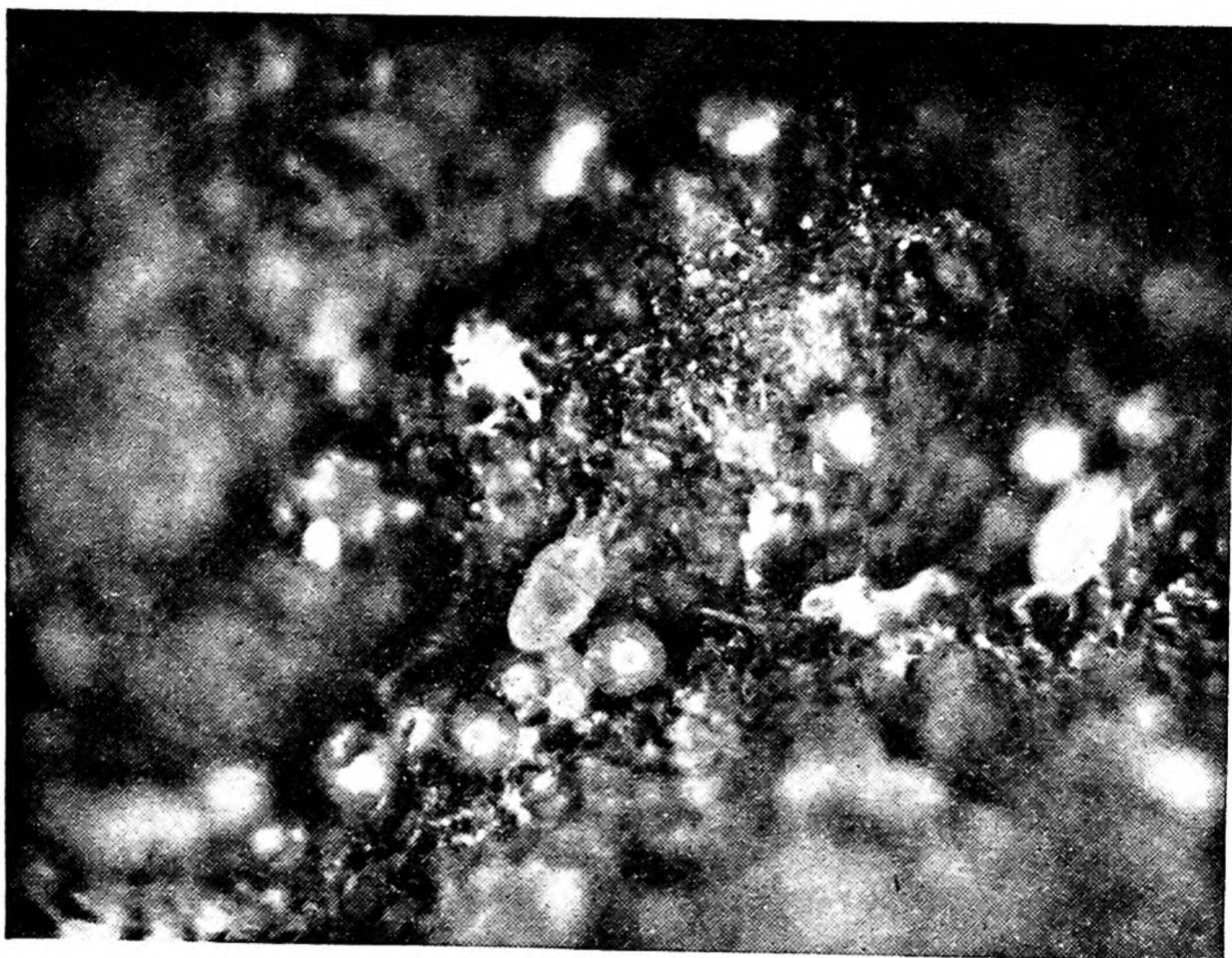


Fig. 19.—Red spider mite and eggs. *A Shell Photograph.*

often increases the effectiveness of the additive insecticide by ensuring intimate contact with, and penetration into, the pest or else by acting as a sticker and enhancing the permanence of the deposit.

Although it has long been recognized that summer petroleum sprays are the most efficient controller of red spider (*Oligonychus ulmi*) on deciduous fruit trees, its use in the United Kingdom has been restricted because of occasional damage shown by leaf and fruit drop which



occurs in circumstances not yet fully understood. The possibility of overcoming this disability by the inclusion of a growth-promoting substance, alpha naphthyl acetic acid, in the spray has been described by Cole and Heeley.<sup>25</sup>

A further drawback to the use of summer sprays in Western Europe is that they are incompatible with lime sulphur washes if applied immediately before or after, though curiously enough, the damage is often less when the two washes are applied simultaneously. Although incompatibility can be avoided by spacing the sprays with a fortnight's interval, this is not always convenient and it can be hoped that the time is now ripe for the discovery of a new and better fungicide which will enable the grower to discard the none too perfect lime sulphur wash.

### **New developments in petroleum oil sprays**

The method of application of plant protectives plays a large role in orchard economics and the dominant trend in much of the developmental work now proceeding is the elimination of labour costs from spray application. To this end, one line of work is leading to the production of high-speed mobile sprayers delivering automatically large volumes of diluted emulsion as they move through the orchard.

Of more interest to this present discussion is the development of petroleum sprays containing only small volumes of water or none at all, thus eliminating the work and cartage associated in conventional sprays with vast volumes of water which form over 90 per cent. of the spray volume. In some forms of apparatus, use is made of an air blast to atomize a concentrated emulsion, or oil alone, into a fast travelling mist which will give the same oil deposit and coverage as that produced by the conventional washes.

Work in a different direction but to the same end has led to the trial of oil fogs, which also contain no water and are produced by vaporizing the oil over a source of heat. In this case, the oil is acting simply as a carrier for an additive toxicant and is selected for its solvent properties and ease of vaporization. The toxicant carried may be pyrethrum, nicotine or D.D.T. and some remarkable results have been achieved in experimental trials using only 4–5 gallons per acre to control larval and adult insects.



These developments are still in the experimental stage, and it is early yet to assume that they will displace conventional washes. However, the incidence of residual insecticides such as D.D.T., benzene hexachloride and chlordane are likely to have a profound influence in future developments and it seems probable that the use of petroleum oils as carriers will largely increase.

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## CHAPTER IX

### COAL TAR DERIVATIVES

COAL tar, produced from the destructive distillation of coal, is a mixture of hydrocarbons chiefly of the aromatic series. From it can be obtained a number of products which exhibit insecticidal action to a greater or lesser degree; those which so far have proved to be of use as economic insecticides are the tar oils or carbolineums and the nitro derivatives of the phenols.

#### Tar oils

The first use of tar oil as an efficient insecticide is recorded by Martin<sup>1</sup> as being at the end of the nineteenth century but for a long time the value of bituminous tar had been known as a wound dressing and wood preservative. The more general use of tar distillate washes for dormant treatment commenced *circa* 1910 and since then they have found favour in Western Europe, but elsewhere their application is limited by the successful competition of the more adaptable petroleum oils.

The source of these oils is coal tar, a by-product in the manufacture of illuminating gas and coke, which on distillation yields a complex mixture of hydrocarbons separated into groups according to their boiling range. As the temperatures at which the distillation "cuts" are made are not standardized throughout the trade, the composition of

TABLE 4

Boiling range	Products
40°—150° C.	Benzene and homologues
150°—210° C.	Phenols and naphthalene
210°—270° C.	Creosote oils
270°—400° C.	Anthracene oils
Residue	Pitch



the distillation group varies somewhat according to the manufacturer; Table 4, quoted from Cunningham,<sup>2</sup> gives representative data of the distillation products which may be obtained from the coal tar.

The groups shown in the table are named after the predominant compounds, but as the *hydrocarbon* classes are represented by homologous series, simple distillation makes no sharp separation and each group is itself a mixture; there are also present small quantities of the same hydrocarbons that are found in petroleum oils but the aromatic series is predominant. The phenol homologues can be removed by treatment with alkalis and are therefore termed "tar acids", while acid treatment likewise removes the "tar bases" which are compounds allied to pyridine and quinoline.<sup>1</sup> The fractions used for insecticidal purposes are taken from the anthracene and creosote oils from which the naphthalene and anthracene are removed by chilling, and the base oil is then standardized as a neutral oil containing a percentage of tar acids.

Tar oils, which are used as water emulsions, show sharp differences in behaviour compared with petroleum oils. They are markedly phytotoxic and thus can only be used as dormant sprays, and whereas they will control the overwintering eggs of *Aphididae* and *Psyllidae*, but not those of red spider (*Acarini*) and *Capsidae*, exactly the reverse holds good for petroleum oils. To explain this differential action, Staniland *et al.*<sup>3</sup> suggested that saturated hydrocarbons of the petroleum oils killed certain eggs by a stifling action while the tar oils contained some ingredient which is chemically toxic to aphid and psyllid eggs. Tutin<sup>4</sup> concluded that the high boiling neutral oil was the factor responsible for high kill and that the removal of the phenol groups increased the toxicity. Kearns *et al.*<sup>5</sup> in subsequent work on the apple aphid (*Aphis pomi*) confirmed that the higher boiling distillates are more effective than those in the lower range and they showed as well that toxicity was associated with the hydrocarbons soluble in dimethyl sulphate. After a critical survey of the known action of tar oils, Martin<sup>6</sup> set a standard for the base tar oils which specifies the content of neutral oil soluble in dimethyl sulphate, the specific gravity and distillation range of the neutral oil and the content of solid matter.

Tar oil washes are prepared as miscible oil concentrates or, for areas which have hard water, as stock emulsion concentrates, and are diluted



in the field to a concentration of approximately 6 per cent. It is necessary to apply them when the tree is in the truly dormant stage, but they give good control of overwintering aphids and psyllids and have excellent tree-cleaning properties. They do not, however, control cap-



**Fig. 20.**—Nymph of apple capsid bug on apple leaf. *A Shell Photograph.*

sids and red spider and their phytotoxicity prohibits their use in spring and summer.



### Nitrophenols

The insecticidal action of phenols and cresols was recognized at an early stage, but though they have found some application as cattle dips and ointments, they have not proved suitable as horticultural and agricultural insecticides. Study of the nitrophenols opened a much more promising field of investigation and some of these form the basis of sprays and dusts in common use to-day.

### Dinitro-ortho-cresol

In a systematic investigation of the ovicidal properties of aromatic hydrocarbon derivatives, Tattersfield *et al.*<sup>7</sup> observed that the introduction of a nitro-group into the phenol molecule resulted in increased toxicity to eggs of *Aphis rumicis* L. and *Selenia tetralunaria* and that the addition of a second nitro-group still further enhanced the ovicidal activity, though the degree was dependent on the relative position of the two nitro groups. The 3.5. dinitro-ortho-cresol proved to be outstanding in ovicidal power and field trials by Gimingham and Tattersfield<sup>8</sup> confirmed the practical value of the discovery. As the dinitro cresol can be incorporated in winter petroleum washes, it has been possible to develop a dual-purpose winter spray, in which the insecticidal action of the oil against red spider, capsids and the winter moth group is supplemented by the ovicidal power of the dinitro cresol against aphids and psyllids, thus obtaining by a single application the pest control which previously necessitated separate sprays of tar oil and petroleum wash.

Barker *et al.*<sup>9</sup> commenting on the fact that many commercial washes are made up with an alkaline emulsifying agent, pointed out that as dinitro cresol is appreciably soluble in water, it migrates from the oil phase to the water phase of the emulsion, according to the partition coefficient, and that the effect increases rapidly with rising pH owing to the formation of cresolates; they showed that at pH4 and below, approximately 90 per cent. of the dinitro cresol is in the oil while at pH11 it is almost completely in the aqueous phase, the most rapid increase in migration occurring between pH4 and pH7. As their biological tests demonstrated that the dinitro cresol in the oil phase was



much more toxic than in the water phase, when tested on the bean aphid, they concluded that to make the most effective use of a winter wash of this type, the *pH* of the diluted spray should not exceed 4.

Dierick<sup>10</sup> reached a similar conclusion when investigating the ovicidal action of dinitro-*ortho*-cresol and its salts. She concluded that the high toxic action must probably be ascribed solely to the undissociated acid molecules and that the cresolate ions and undissociated salt molecules have little or no ovicidal effect. An interesting observation of hers is that when dinitro-*ortho*-cresol is incorporated in petroleum oil emulsions, the *pH* value not only affects the resultant kill, but the total effect is either greater or less, according to whether the media is acid or alkaline, than would be expected from the consideration of the toxicity of the two components assessed separately. In spite of this work, however, the majority of dinitro cresol washes to-day are stock emulsions, often made up with alkaline emulsifiers, and contain no buffers to offset dilution in the field with alkaline water; they give good control over the overwintering common pests of deciduous trees when properly used, but it seems possible that future developments will be towards the acid type of emulsion or "oil-fixed" dinitro cresol in which the *pH* is controlled, even after final dilution, to prevent migration of the dinitro cresol into the water phase.

On the European continent, tar oil has been well established for a number of years; recently the use of dinitro-*ortho*-cresol or its salts, as a suspension or solution in water, has become popular as a substitute for tar oils. Such products are not only cheaper than tar oils but the latter have been in short supply, thus forcing the grower to try the new substitute; it remains to be seen, however, whether these preparations will continue in favour now that tar oils and dinitro cresol petroleum emulsions are once more available. There is also a limited application for dinitro cresol as a dust, carried in an inert diluent, where it can be applied to the plant in dormant or delayed dormant stage or where burning of the vegetation does not matter. Thus apple-blossom weevil can be controlled by a dust of this type though D.D.T. preparations have largely superseded it. Dinitro cresol dust also showed outstanding promise as a contact poison for locusts, but extensive field trials have shown certain application difficulties, and research is now directed to

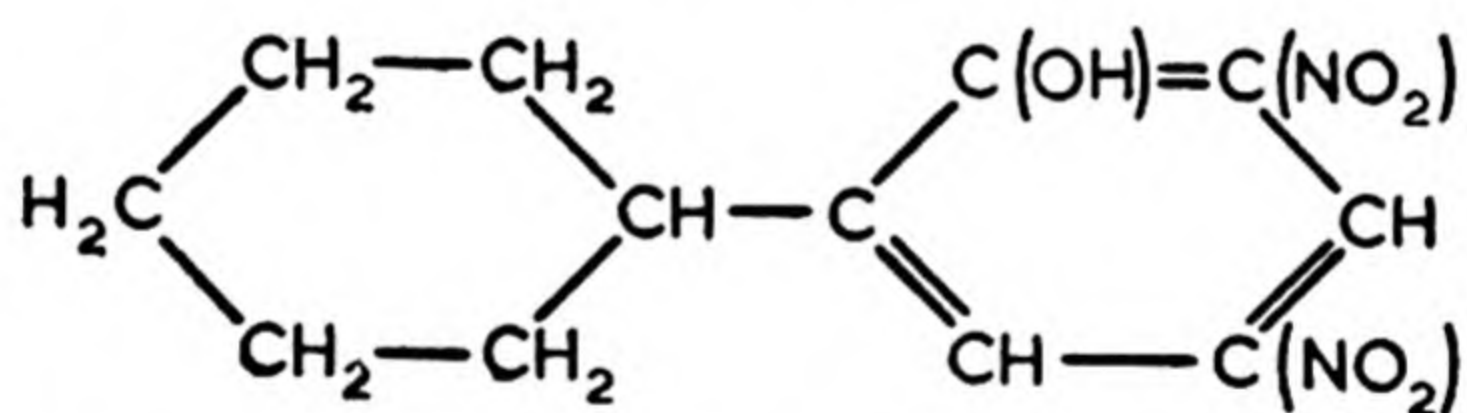


the application of the dinitro cresol in organic solvents which, it is hoped, will aid penetration through the insect cuticle.

### Dinitro-*ortho*-cyclohexylphenol

Although dinitro-*ortho*-cresol has proved to be a powerful weapon for insect control, it is limited to application in the dormant or late dormant stage of the host plant as its phytotoxicity precludes its use on foliage or fruit. Search through the nitrophenol group for a control material which could be safely applied as a summer spray or dust led to the investigation of dinitro-*ortho*-cyclohexylphenol and its salts.

Dinitro-*ortho*-cyclohexylphenol, known commonly as DNOCHP, is a practically odourless, yellowish-white crystalline solid of melting point 106° C. It is soluble in many of the common organic solvents while its solubility in water is largely determined by the *pH* value. The presence of the two nitro groups confers a more definite acidic character to the *cyclohexylphenol* and well defined salts can be formed with inorganic bases, amines, and heterocyclic bases.



DINITRO-ORTHO-CYCLOHEXYLPHENOL

Fig. 21

Kagy<sup>11</sup> observed that DNOCHP and some of its salts were effective stomach poisons to lepidopterous larvae and Kagy and Richardson<sup>12</sup> demonstrated control of *Aspidiotus perniciosus* and *Anuraphis roseus* and other insects, when it was incorporated in dormant oil sprays, and acted apparently both as a contact and a stomach poison. Boyce *et al.*<sup>13</sup> in comprehensive studies on the insecticidal and phytocidal properties of this compound found that the distribution of DNOCHP between the two phases of an oil-water emulsion depends on the *pH* value and that the greatest insecticidal effect is obtained when the *pH* of the diluted spray does not exceed *pH* 5 at which value the toxicant is



concentrated almost entirely in the oil. They obtained promising results from DNOCHP incorporated in dormant sprays, but although some trials showed that it could be used against scale pests and red spider (*Paratetranychus citri*) on citrus with only moderate damage to the plant, it was concluded that the margin of safety between the concentration of the compound in summer oil required to given insect control and that which causes tree injury was so narrow that its use with petroleum oil on citrus could not be recommended. They found that colloidal suspensions of DNOCHP and solutions of its salts, notably the triethanolamine salt, in water all gave promising results as controllers for citrus pests.

Boyce *et al.*<sup>14</sup> obtained successful economic control over red spider (*Paratetranychus citri* and *Tetranychus telarius*) by means of a dust compounded of 1 per cent. DNOCHP in walnut flour, which diluent remains completely inert to action by the acid. This mixture, known commonly by the proprietary name of "DN" dust can be used with comparative safety on citrus provided that the temperature does not rise above 95° F. On deciduous trees, where it can be used for the control of red spider and the clover mite (*Bryobia practiosa*), tree tolerance appears to be greater, and it is also applied to cotton and hops for control of mites.

Simpson<sup>15</sup> demonstrated that the phytotoxic effect of the dinitro-cyclohexylphenol can be diminished by the use of its dicyclohexylamine salt without impairing its properties as an insecticide or acaricide. This latter preparation, made as a proprietary spray and dust, has made some headway in England for the control of red spider on hops and glasshouse crops and it is claimed that it exerts a selective action, killing the mites but not their predators which are thus enabled to control any remaining infestation. The dicyclohexylamine-dinitro-cyclohexylphenol salt still retains some phytotoxic action and due regard must be paid to prevailing temperatures at the time of application.

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## CHAPTER X

### MISCELLANEOUS INSECTICIDES

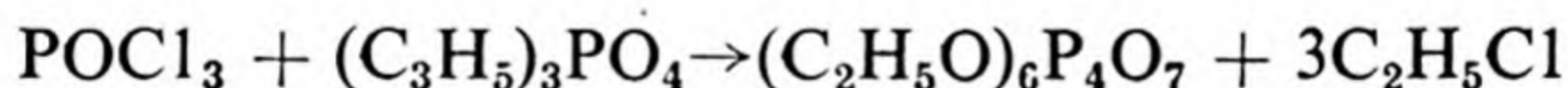
THE selection of the materials mentioned in this chapter has been based mainly on their special interest as recent developments.

#### Hexaethyl tetraphosphate

Hexaethyl tetraphosphate,  $C_{12}H_{30}O_{13}P_4$ , is of recent origin and was used in Germany during the second world war under the name "Bladan". This insecticide consisted of 60 per cent. of hexaethyl tetraphosphate, 20 per cent. wetting agent and 20 per cent. of a solvent such as xylol.<sup>1</sup>

It was prepared in Germany by the reaction of 1 mol. of phosphorous oxychloride with just over 3 mols. of triethyl phosphate, the two compounds being blown to the top of a column (packed with Raschig rings) fitted at the bottom with a reaction kettle, the system being kept at 30 atmospheres pressure and 140° C.

The product flowed to a cooler of lead coil.<sup>1</sup>



Hexaethyl tetraphosphate is a light amber coloured liquid, specific gravity 1.28 (approximately), solidifies at -40° C. and decomposes at temperatures above 150° C. It is miscible in all proportions with water, acetone, alcohol, ether, diacetone alcohol, ethyl acetate, glycerol, chloroform, chlorobenzene, carbon tetrachloride, benzene, toluene, xylene and alkyl naphthalenes but is insoluble in kerosene.<sup>2</sup>

At ordinary temperatures and in the absence of moisture, hexaethyl tetraphosphate is apparently stable, no change in refractive index or density being observed after six months. When diluted with water it is partially hydrolysed to yield intermediate products the nature of which have not yet been determined.<sup>2</sup>



Recent tests have shown that hexaethyl tetraphosphate in the absence of water does not appreciably corrode brass or iron but aqueous solutions of this insecticide rapidly attacked galvanized iron, iron was attacked at a much slower rate and brass is not attacked appreciably.<sup>2</sup>

In preliminary experiments<sup>2</sup> Bladan mixture, pure hexaethyl tetraphosphate, Bureau mixture (a preparation similar to Bladan containing as emulsifier a proprietary glycol monoisooctyl phenyl ethyl ether), nicotine alkaloid and nicotine sulphate were compared for the control of the cabbage aphid (*Brevicoryne brassicae*) and the pea aphid (*Macrosiphum pisi*). The results are summarized in Tables 5, 6 and 7:

TABLE 5

Results of tests with hexaethyl tetraphosphate and nicotine dust mixtures against the cabbage aphid at an average temperature of 67° F. All materials contained 3 per cent. of the toxicant.				
Series 1. Single cabbage leaves treated. Dosage 750 mg. of dust.				
Treatment	Fresh dust mixtures		Aged dust mixtures <sup>1</sup>	
	Number of aphids	Per cent. mortality in 24 hrs.	Number of aphids	Per cent. mortality in 24 hrs.
Hexaethyl tetraphosphate:				
Bladan-talc .. .. .	275	100	200	0
Pure material-talc .. .. .	375	100	100	87
Nicotine sulfate-hydrated lime	450	98	—	—
Check, untreated .. .. .	380	0	—	—
Series 2. Entire cabbage plants treated. Dosage 2 g m. of dust.				
Hexaethyl tetraphosphate:				
Pure material-talc .. .. .	225	100	900	50
Pure material-hydrated lime	850	95	600	15
Nicotine sulfate-hydrated lime	250	60	—	—
Check, untreated .. .. .	950	0	—	—
<sup>1</sup> Aged dust mixture used in Series 1 was seven to ten days old, that in Series 2 was two to five days old.				



TABLE 6

*Results of tests with atomized aqueous solutions of hexaethyl tetraphosphate (Bureau mixture) and nicotine against the cabbage aphid on potted cabbage plants, at an average temperature of 68° F. Dosage 5cc. per plant.*

Treatment	Per cent. of toxicant	Number of aphids	Per cent. mortality in 24 hrs.
Hexaethyl tetraphosphate .. ..	0.6	1,000	88
	1.2	800	90
	2.4	1,200	92
Nicotine sulfate <sup>1</sup> .. ..	0.4	1,000	8
	0.8	800	13
Check, untreated .. ..	—	275	0

<sup>1</sup> The emulsifier (polyethylene glycol monoisooctyl phenyl ethylether) employed in the Bureau mixture was also used in this preparation.

Bronson and Hall<sup>2</sup> concluded that, "On the basis of these preliminary greenhouse tests it is evident that freshly mixed hexaethyl tetraphosphate dust mixtures offer promise for cabbage aphid control. The exact length of time that they can safely be stored before use must be determined by preparing larger quantities and testing them under field conditions.

"Hexaethyl tetraphosphate may deteriorate more rapidly in solutions than in dust mixtures, but since solutions are customarily applied as soon as prepared or diluted for use, it is believed that they may prove to be more satisfactory than dusts.

"It should be emphasized that in these tests the solutions were atomized into a chamber at temperatures slightly below 70° F. and allowed to settle onto the aphids which were not wetted as with conventional sprays. This evidently accounts for the unusually low mortalities obtained with nicotine solutions."

Later, Hall and Jacobson<sup>3</sup> reported that hexaethyl tetraphosphate is a non-distillable liquid mixture of empirical composition  $(C_2H_5)_6P_4O_{13}$ , composed essentially of tetraethyl pyrophosphate and ethyl metaphosphate with pentaethyl triphosphate as a possible third constituent.



TABLE 7

<i>Results of tests with hexaethyl tetraphosphate and nicotine solution and dust mixtures against the pea aphid on potted pea plants at average temperature of 68° F. Dusts freshly mixed with talc, dosage 2 grams per plant. Dosage of solution 5 cc. per plant.</i>			
Treatment	Aqueous solutions		
	Per cent. of toxicant	Number of replicates	Per cent. mortality in 24 hrs.
Hexaethyl tetraphosphates	0.6	8	8
Bladan .. .. .	0.6	8	8
Bureau mixture .. .. .	0.3	4	7
	0.6	20	54
	1.2	16	89
	2.4	4	94
Nicotine alkaloid .. .. .	1	12	4
	2	8	3
Check, untreated .. .. .	—	8	0
Dust mixtures			
Hexaethyl tetraphosphate:			
Bladan .. .. .	3	8	36
Pure material .. .. .	3	12	99
Bureau mixture .. .. .	3	12	90
Check, untreated .. .. .	—	16	0

These authors prepared distillable tetraethyl pyrophosphate by two other methods and also isolated the compound from nondistillable products including the so-called hexaethyl tetraphosphate. The tetraethyl pyrophosphate was three to five times as active against insects as hexaethyl tetraphosphate and appears to be the active ingredient of the non-distillable products described. As a result of this work, there has been some suggestion that the insecticidal action of H.E.T.P. should be fortified by the addition of a proportion of tetraethyl pyrophosphate; this, however, is likely to increase the hazards to human health in applying the insecticide.

While there is now a considerable body of evidence to show that hexaethyl tetraphosphate is an excellent aphicide and can successfully



replace nicotine for this purpose, much less is known about its action on other insects. Preliminary investigations have indicated that it gives good control over red spider adults but that its killing power on the mite eggs is weak. It is too early to say what place this insecticide will finally assume in the field of plant protectives but it appears likely to become a stop-gap substitute for nicotine, while the latter is in world short supply. It may eventually be displaced by still newer insecticides.

### Azobenzene

Azobenzene has been known to science for at least a hundred years, but although its insecticidal properties were suspected, no thorough tests were possible until recent years as a suitable method of application had not been discovered. Now that the initial work of perfecting suitable methods of applying this substance to plants, without causing economic damage, has been accomplished, it can be expected that rapid developments will take place in the near future, especially in the control of pests in the glasshouse.

Azobenzene,  $C_{12}H_{10}N_2$ , is an orange-red powder with a melting point of  $68^{\circ}C$ . and boiling point of  $293^{\circ}C$ . It is insoluble in water but is easily dissolved in organic solvents such as kerosene and acetone. It can be prepared by the reduction of nitrobenzene in boiling methanolic sodium hydroxide solution to which is added a calculated amount of zinc.

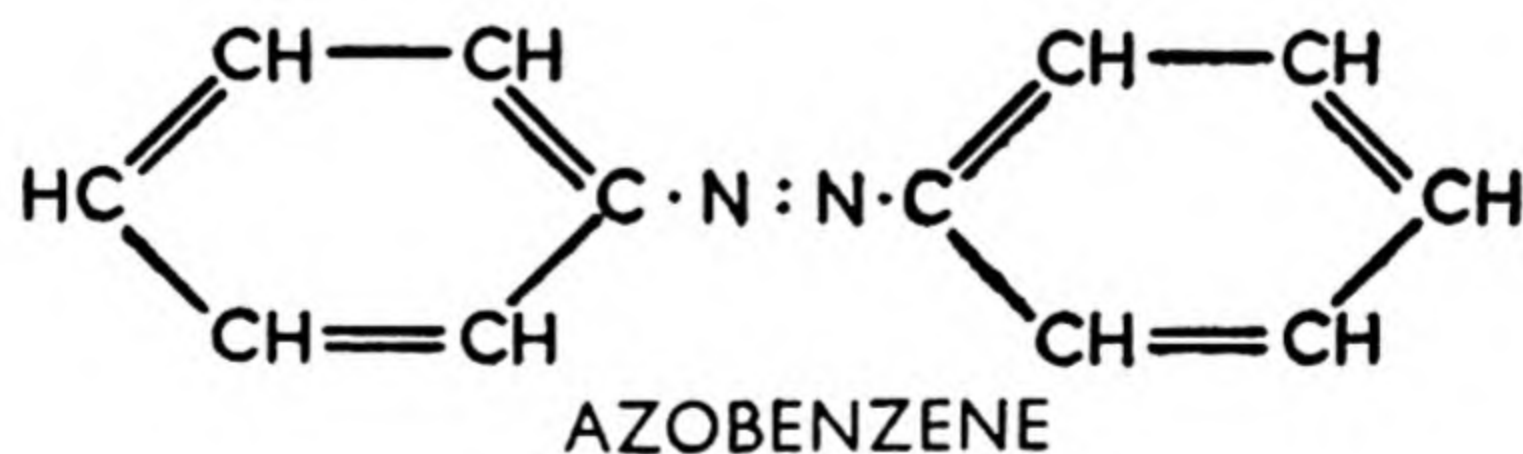


Fig. 22

Haring<sup>4</sup> tested dusts composed of azobenzene and inert diluents and reported satisfactory results over a number of pests including Colorado beetle and red spider. A field trial, using 20 per cent. azobenzene in whiting dust at the rate of 30 lb. per acre, resulted, after two separate treatments at seven days' interval, in a count of 62 per cent. ears of corn free of cornborer damage, whereas a duplicate trial using unspecified



commercial insecticides gave only 42 per cent. of clean ears. A mixture of 20 per cent. active material in bentonite dust proved successful against red spider on glasshouse carnations and caused no foliage damage, although some of the outer petals were burned. Further experiments by the same worker showed that, on carnations, virtually complete red spider control could be obtained with concentrations as low as 5 per cent. when whiting powder was the carrier.

Blauvelt,<sup>5</sup> concentrating on methods of using this insecticide in the most simple manner for glasshouse crops, recommends the use of a wettable powder containing 70 per cent. azobenzene applied as a paste to the steam pipes at the rate of 1 lb. of paste for every 40,000 cubic feet of space. The heat of the pipes volatilizes the azobenzene which then acts as a fumigant and reaches all parts of the glasshouse without further effort on the part of the grower. It is noteworthy that the azobenzene kills red spider eggs as well as the mature and larval forms and that controls of 99.9 per cent. have been obtained over all stages of this pest on roses and other floral crops.

The use of azobenzene as a paste applied to steam pipes for the control of red spider in glasshouses has gained considerable popularity in the United States. Certain somewhat exacting conditions must be fulfilled to avoid plant injury but these are of small weight compared with degree of control obtained. During the fumigation, the temperature must be maintained close to 75° F. and any marked drop in temperature must be avoided to prevent foliage injury. After treatment, the houses should be ventilated slowly with steam full on so that cooling takes place gradually; in cold weather, it is necessary to carry out the fumigation in the daytime when these conditions can be more easily fulfilled. Reduction in the colour of buds is more common than leaf injury and is more likely to appear when treatment is carried out in cloudy weather.

In England, Hey<sup>6</sup> has confirmed the findings of the American workers and shown that pastes made from a wettable powder containing 50 per cent. azobenzene and applied at concentrations of 0.1 per cent. active material will successfully control red spider on hydrangeas, roses and vines. He obtained complete control over the red spider infesting apple, but a few days after treatment, severe and extensive foliage scorching



appeared and it seems probable that a completely different type of formulation will be necessary before azobenzene can be successfully used on this crop.

The most interesting aspect in the recent work on azobenzene has been its association with the development of a new method of application of insecticides for the control of glasshouse pests. The use of a paste, made from an azobenzene wettable powder placed on steam pipes for subsequent volatilization, is impracticable in Great Britain where the usual source of warmth is by a hot-water system that is not suitable for this practice. In an endeavour to discover a simple and effective applicational method which will not entail the use of skilled labour for long periods, attention has been paid to the development of an aerosol.

There are certain principles governing the effectiveness of an aerosol as an insecticide and one of the most important relates to particle size. It has been found that aerosols having a particle size of 0.5 to 30 microns diameter are the most effective, as those composed of particles smaller than these dimensions are unable to penetrate the protective coverings often surrounding insect pests, while those comprising larger particles are spaced too widely and do not give adequate coverage. The composition of the liquid solvent also affects the nature of the aerosol and certain of them are more rapidly dispersed, as, for instance, those containing a high boiling aromatic petroleum solvent composed mostly of alkylated naphthalenes; methylene chloride and acetone also disperse readily to give aerosols of suitable particle size.

Goodhue and others,<sup>7,8</sup> in research on the factors governing the particle size of an aerosol, found that the addition of a non-volatile liquid such as dibutyl phthalate or sesame oil, to the volatile solvent altered the resultant particle size in direct proportion to the amount incorporated; by adjusting the percentage of non-volatile ingredient he was therefore able to obtain aerosols with the desired droplet size. He also studied the effect of different types of nozzles and concluded that a better dispersion is obtained when the liquid at the nozzle exit "boils" as the propellant gas, which is partially dissolved in the solvent while under pressure, escapes into the atmosphere.

Working on similar lines, Cakebread and Whitlock<sup>9</sup> have developed



a practical form of applicator embodying the principles indicated. The apparatus consists essentially of a container for azobenzene dissolved in an organic solvent such as acetone which can be charged under pressure with carbon dioxide, utilizing a "sparklet" bulb, the gas partially dissolving in the solution. By releasing a trigger, the pressure of the carbon dioxide forces out of a small aperture the liquid, which, boiling violently as the dissolved gas escapes, is dispersed as a finely divided spray. Within a short distance from the nozzle, the solvent evaporates leaving the azobenzene suspended in the air as a true aerosol with a particle size of 2 to 10 microns diameter. These particles consist of liquid azobenzene and not crystals, and their size is controlled by the addition of sesame or rape oil.

While some workers contend that the insecticidal action in this instance is due, at least in part, to the liquid particles of azobenzene coming into direct contact with the insect, other opinions suggest that the azobenzene is acting purely as a fumigant and that atomization merely facilitates volatilization of the compound.

Utilizing this method in certain trials, these workers have demonstrated complete control over all stages of red spider attacking tomato plants and no phytotoxic effect occurred. It is still too early to estimate the full value of this manner of utilizing azobenzene in the glasshouse and a full assessment must await more extensive use. The method, however, is of great interest and is already being developed for use with other insecticides such as D.D.T. and nicotine.

### Sabadilla

That sabadilla possessed insecticidal properties was known as long ago as 1572,<sup>10</sup> but it was not until 1938 that the thorough investigation of these properties began.

Sabadilla is a plant of the *Liliaceae* family, tribe *Veratreae* and belongs to the genus *Schoenocaulon*. There are about twenty species of this plant, growing as a non-cultivated crop in the United States, Mexico and South America.

The liquid form of the insecticide is prepared by extracting the powdered seed with highly refined kerosene, in the proportion of about 0.5 lb. of powdered seed to 1 gallon (U.S.) of solvent, for approximately



one hour at 150° C.<sup>11</sup> Later experiments<sup>12</sup> showed that by treating the powdered seeds with an alkali (such as lime) prior to extraction with kerosene, it was possible to reduce the extraction temperature to 60° C. This method yielded a product that was almost as effective as that obtained by extracting the untreated seed at 150° C. Allen and Dicke<sup>13</sup> reported that the addition of 1 per cent., by weight, of lethane to sabadilla solution had a synergistic\* action.

Sabadilla dusts are prepared by heating coarsely ground seeds for four hours at 75° C. to 85° C., or alternatively, by treating the coarsely ground seed with alkali. The seeds are then finely powdered with a diluent such as talc or sulphur.

The alkaloids present in sabadilla (having the group name of veratrine and totalling about 0.3 per cent. of the dried ripe seeds) are: sabadine,  $C_{29}H_{50}O_8N$ , melting point 238–240° C.; sabadilline,  $C_{34}H_{53}O_8N$ , melting point, about 200° C.; sabadinine (cevine)  $C_{27}H_{34}O_8N$ , melting point, about 160° C.; cevadine (veratrine),  $C_{32}H_{49}O_9N$ , melting point, about 205° C. and veratridine,  $C_{36}H_{51}O_{11}N$ , melting point 180° C.

Ikawa and co-workers<sup>14</sup> reported that the alkaloids present in sabadilla seeds were responsible for the toxicity of the kerosene extracts of the ground seed to the housefly (*Musca domestica*). They found that veratridine was highly toxic, cevadine being less toxic; veratridine at 20 mg. per 100 mil. of solvent and cevadine at 42 mg. per 100 mil. gave practically complete knockdown in three minutes. Both alkaloids, as well as the remaining alkaloid mixture, gave very quick knockdown of the insects. Sabadinine appeared to be non-insecticidal. The oil extracted from the seeds gave a knockdown but possessed no killing properties.

The total alkaloids present in sabadilla are only partially soluble in kerosene and Allen and co-workers<sup>15</sup> reported experiments carried out to determine the toxicity of these alkaloids in dust suspensions, using the milkweed bug (*Oncopeltus fasciatus*) and the red-legged grasshopper (*Melanoplus femur-rubrum*) as test insects. They concluded that cevadine was the most toxic constituent, veratrine and veratridine were

\* Synergism, increased effect due to the addition of a substance where the total effect is greater than the sum of their separate effects.



considerably less toxic and cevine was non-toxic to the insects at the concentrations used (from 1 : 100 to 1 : 1,000). The concentration of cevadine required to give a 50 per cent. mortality of the milkweed bug was 1 to 8,000, a concentration of 1 in 2,000–3,000 was necessary to give a 50 per cent. mortality of the red-legged grasshopper. The concentration of cevadine in kerosene solution to give a 50 per cent. mortality of the milkweed bug was 1 in 2,000.

Experiments reported by Allen and co-workers<sup>10</sup> showed the necessity of storing kerosene extracts of sabadilla seed in tightly-capped dark brown bottles. Samples of the extracts deteriorated rapidly when exposed to light. Samples of the same extracts that had been stored for periods of twelve to twenty-two and a half months at room temperature showed a cloudy precipitate which was filtered off before the samples were tested. The results obtained showed that no appreciable change in toxicity had occurred.

Recent preliminary field experiments<sup>16</sup> have shown that a 10 per cent. sabadilla dust, containing 0.2 per cent. alkaloids, reduced a high percentage of nymphs and adults of the squash bug (*Anasa tristis*), a 30 per cent. dust, containing 0.8 per cent. alkaloids, gave a 96 per cent. mortality in seventy-two hours as against 1.1 per cent. in the controls.

Tate and Gates<sup>17</sup> tested sabadilla dusts and sprays against the chinch bug (*Blissus leucopterus*) and the squash bug. A 3 per cent. and a 5 per cent. dust gave mortalities of 80 per cent. and 98 per cent. respectively after two days against the chinch bug, the percentage mortality in the control was 2.1 per cent. Sprays containing 0.5 lb., 1 lb. and 2 lb. per 100 gallons (U.S.) of solvent gave mortalities of 45.6 per cent., 65.4 per cent. and 99.4 per cent., respectively against the chinch bug, the per cent. mortality in the control was 3.9. Against the squash bug, dusts containing 5 and 10 per cent. sabadilla and sprays containing 2 lb. and 4 lb. of sabadilla per 100 gallons (U.S.) gave the following per cent. mortalities respectively, 85, 96, 90 and 99. The average mortality in the controls was less than 2 per cent.

Brunn and Allen<sup>18</sup> reported that sabadilla dusts and sprays compared favourably with rotenone and calcium and lead arsenate for the control of the cabbage worm (*Pieris rapae*) and the cabbage looper (*Autographa brassicae*).



Fisher and Allen<sup>19</sup> reported that a dust containing 10 per cent. sabadilla, 10 per cent. lime and 80 per cent. sulphur reduced the number of potato leafhoppers (*Empoasca fabae*) infesting string beans by 97.8 per cent. A 10 per cent. sabadilla, 10 per cent. lime and 80 per cent. talc dust reduced the percentage of leafhoppers by 88.9 per cent. The dusts were applied at the rate of 35 lb. per acre.

A dust containing 20 per cent. sabadilla, 20 per cent. lime and 60 per cent. pyrophyllite applied at 30 to 35 lb. per acre reduced the percentage of potato leafhoppers, tarnished plant bugs and grasshoppers on alfalfa by 90.6, 97.6 and 97.6 per cent. respectively. A similar trial using a dust containing 10 per cent. sabadilla, 10 per cent. lime and 80 per cent. of sulphur gave the following figures respectively, 95.5, 93.7 and 97.7.

**Toxicity to warm-blooded animals.** Toxicity tests<sup>12</sup> against warm-blooded animals, using rats as test animals, showed that while sabadilla dusts caused temporary irritation, the growth of the rats was almost normal during the treatment and death did not ensue at the concentrations investigated. On the other hand, rotenone dusts caused injury to the eyes and the rats failed to gain weight. In another series of experiments<sup>12</sup> the toxicity of heat-treated sabadilla seeds, the isolated crude sabadilla alkaloids, rotenone and D.D.T. was compared by incorporation in the basal ration of the rats. D.D.T. was the most toxic, 0.625 per cent. in the diet causing extreme restlessness and tremors, death resulting in three to five days.

Rotenone, at the same level of intake, caused restlessness, death resulting in seven to nine days. The toxic level for sabadilla seed was slightly less than 2.5 per cent. and for the isolated alkaloids in excess of a 2.5 per cent. equivalency. These observations were considered to indicate that whilst sabadilla seed is irritating and toxic to warm-blooded animals, its toxicity is less than that of rotenone or D.D.T.

### Ryanex

It has recently been discovered<sup>20</sup> that plants of the genus *Ryania* contain alkaloids which possess insecticidal properties and that extracts and concentrates derived from these plants can be used as insecticides and



insect repellents. The concentrates were stated to be tan-coloured amorphous powders, soluble in a variety of solvents, and to be highly effective against such insects as cockroaches, plant bugs and aphids, beetles and lepidopterous larvae.

Pepper and Carruth<sup>21</sup> reported extremely effective control of the European cornborer (*Pyrausta nubilalis*) under field conditions in New Jersey and New York with "Ryanex" prepared from the tropical plant *Ryania speciosa* Vahl.

### The Fluorine compounds

The fluorine compounds have long been known for their insecticidal properties and in recent years have attained some popularity as stomach poisons to replace lead arsenate. Fluorine occurs extensively in nature as fluor-spar,  $\text{CaF}_2$ , as cryolite,  $\text{Na}_3\text{AlF}_6$ , and constitutes a large percentage of the waste from the treatment of rock phosphate to produce fertilizer.

The first compound to be extensively used for the control of insects was **sodium fluoride**,  $\text{NaF}$ , which found application as an exterminator of household pests and later for the treatment of poultry to control lice. It is a heavy white powder, of specific gravity 2.77 and is used as a dust, chiefly against cockroaches, when it appears to act both as a stomach and contact poison; its contact effect, however, may be due to ingestion when the insect cleans its antennae and legs by drawing these across the mandibles. It dissolves in water forming a phytotoxic solution and is therefore precluded from use as a horticultural spray.

**Sodium fluosilicate** (sodium silicofluoride),  $\text{Na}_2\text{SiF}_6$  has a wider application<sup>22</sup> as a plant protective when it is usually applied as a dust or as a bait. It is sparingly soluble in water and is liable to cause plant injury, probably due to reactions with impurities in the preparation or with plant excretions<sup>23</sup> with the subsequent release of sodium fluoride. It can, however, be used with comparative safety in semi-arid areas where dews do not occur and is, at present, a widely used plant protective in the Middle East for the control of the grape berry moth on table grapes, and for the protection of fodder crops against cutworms of *Agrotis* and *Laphygma* species. Sodium fluosilicate can also be used in bran baits for the control of locusts and cutworms and it has been suggested that



such baits would be less dangerous to stock and humans than the usual sodium arsenite bait; as, however, it is necessary to use double the amount of the fluosilicate, as compared with the arsenical compound, to obtain the same effective kill, it is doubtful whether any advantage can be gained. Sodium fluosilicate is widely used as a moth-proofing agent as it is readily absorbed by wool.

**Barium fluosilicate**,  $\text{BaSiF}_6$  is a white crystalline powder, relatively insoluble in water and very toxic to insects. Because of its low solubility, it can be used as a stomach poison with little danger of plant damage and has found considerable favour as a general insecticide against chewing insects as a substitute for lead arsenate. In Palestine, its use for the control of *Polychrosis botrana* has become so common, that "barium" has now become an Arabic word. Although originally proposed as a substitute for lead arsenate because of its less poisonous properties to humans, some doubt has now arisen as to the chronic effects of continual small doses which may be left as residues on fruits and vegetables.<sup>24</sup> While barium fluosilicate can be used on table grapes, it is not applied to wine grapes because of the residues which find their way into the wine.

**Sodium fluoaluminate**,  $\text{Na}_3\text{AlF}_6$  or  $\text{Al}_3.3\text{NaF}$ , occurring naturally as cryolite, can also be prepared synthetically by the reaction of aluminium fluoride, ammonium fluoride and sodium chloride. The synthetic product is a lighter powder than the naturally occurring mineral, and is more suitable for the preparation of insecticidal dusts and suspensions, although both forms have found wide application. The original trials of cryolite as a plant protective were due to Marcovitch and Stanley<sup>25</sup> who concluded that although it was less toxic than barium fluosilicate, it nevertheless gave satisfactory control over the Mexican bean weevil and at the same time is considerably cheaper. Only slightly soluble in water, it can be applied to many plants without serious injury but has proved phytotoxic on some crops. It has been used with some success for the control of codling moth and also has been extensively applied as a dust from aeroplanes for the protection of fodder crops. Like the majority of fluorine compounds, it is incompatible with alkaline plant protectives and therefore cannot be used in conjunction with lime sulphur or Bordeaux mixture.



Many other simple and complex salts of fluorine with metals have been shown to possess toxicity to insects but none of them have found any wide application, though some can be used for special purposes, for example, magnesium fluosilicate as a wood preservative.

### Sulphur and Sulphur Compounds

While sulphur and its compounds have found wide application as fungicides, their use as insecticides is very limited and confined to the control of only a few pests of which mites and certain scale insects are the most important. A large volume of work has been directed to the investigation of the action of these compounds, but as most of it is in relation to their fungicidal activity, only a brief account is given here.

Free sulphur occurs in the volcanic areas of the world, and was well known to the ancients who, however, only recognized the toxic action of burning sulphur. Although the beneficial effect of sulphur in controlling parasitic mites infesting animals had been known for some considerable time, its use on a large scale as a plant protective probably dates only from the latter half of the nineteenth century.

Originally, the form of sulphur most widely used for acaricidal or insecticidal purposes was "flowers of sulphur" obtained by the sublimation of the crude element. It was then demonstrated that there was a direct relationship between the degree of toxicity and the particle size<sup>26</sup> which has resulted in the preparation of more finely divided powders by grinding or by precipitation in which a colloidal suspension in water can be obtained. When applied as a dust, some advantage can be gained by the addition of fillers such as talc or gypsum to make the powder flow more freely<sup>23</sup> but such mixtures are not commonly used; for use as sprays, it is necessary to include a wetting agent to obtain an even suspension and supplements are sometimes added to increase the tenacity of the deposit.

Sulphur is most widely used for the control of mites on citrus and other plants such as gooseberry and blackcurrent; it will also control certain species of thrips, *e.g.* citrus thrips. The most effective use of sulphur is in the sub-tropics where, presumably, volatilization more readily takes place than in temperate zones; at temperatures above



30° C., however, care must be taken as damage to plants may occur as sulphur scald. Many of the preparations for the control of mites parasitic on animals have sulphur as the active agent, and though these may be applied either as ointments or baths, it appears that the controlling action is by particulate sulphur.

**Lime sulphur** is a complex mixture of calcium thiosulphate and calcium polysulphides produced by boiling a suspension of calcium hydroxide with sulphur. Originally used as a sheep dip, it was accidentally discovered in 1886 that it would also control the San José Scale (*Aspidiotus perniciosus*)<sup>24</sup> as a result of which it rapidly established itself as the standard insecticide for this purpose. The early lime sulphurs were home-made products and at first made in a strength suitable for direct application which was made while the solution was still warm; as an improvement on these, a lime sulphur concentrate was evolved which was suitable for dilution with water to field strength while a third method utilized the heat produced by the slaking of the lime to form "self-boiled lime sulphur".<sup>27</sup> The concentration of the polysulphides varied at each making and it was necessary to utilize a hydrometer in order to arrive at the correct amount of additional water to make a spray of standard strength. To-day, lime sulphur concentrates are factory-made and are sold at a guaranteed strength indicated by the specific gravity.

Lime sulphur is used for the control of mites on citrus and other plants and is also widely used as a sheep dip against scab (*Psoroptes communis*). Martin<sup>24</sup> has briefly reviewed the theories of its toxic action which he ascribes to the polysulphides or to the sulphur formed by their decomposition. Lime sulphur can cause "sulphur scald" if applied at high temperatures and there are also certain "sulphur-shy" varieties of plants on which neither lime sulphur nor sulphur can be applied with safety.

### Parathion

Since the manuscript for this book was prepared, the results of preliminary tests with a new insecticide, "Parathion" or "Thiophos 3422" have been published.



During World War II Schrader,<sup>28</sup> working on organic phosphorus insecticides, investigated the compound *OO* diethyl-*o*-*para*-nitrophenyl-thiophosphate which he termed E 605. Schrader's observations on the remarkable toxicity of this chemical were confirmed and it is now being manufactured commercially in a number of countries under the general name Parathion.

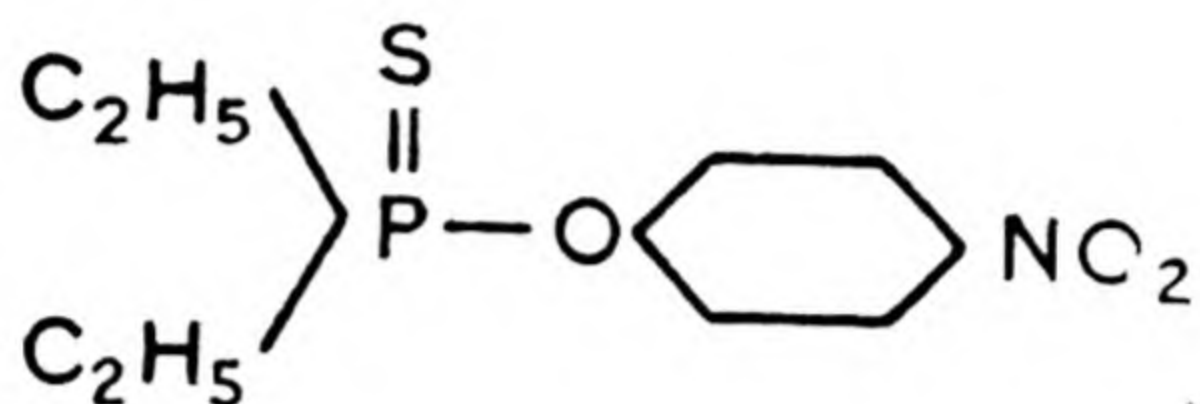


Fig. 23

Parathion is a liquid varying in colour according to preparation from water-white to dark brown, with a boiling point of  $375^{\circ}\text{C}.$ , a specific gravity of 1.26 at  $25^{\circ}\text{C}.$  and a vapour pressure of approximately 0.0006 Hg at  $24^{\circ}\text{C}.$ <sup>29</sup> It is soluble in water to the extent of 20 p.p.m. and, while relatively stable in aqueous solution or in lime-water solution, it hydrolyses in alkaline solutions to *para* nitrophenol and diethyl *ortho* thiophosphoric acid.<sup>30</sup> Its preparation by Schrader was first by reacting sodium ethoxide and phosphorus sulphochloride in alcohol at  $-5^{\circ}\text{C}.$  and then treating the resulting product ( $(\text{CH}_2\text{H}_5\text{O})_2\text{PSCl}$ ) with sodium *para* nitrophenate in chlorobenzene at  $120^{\circ}\text{C}.$

The manufactured product contains about 75 per cent. of the pure chemical. Commercial concentrates have been formulated as wettable powders containing 5 to 50 per cent. active material and also as a miscible oil preparation containing approximately 70 per cent. Parathion and 30 per cent. emulsifier. The concentration of active material applied in the field varies from 0.1 to 0.01 per cent. but against certain insects even lower concentrations have been reported to give satisfactory control.

Parathion acts as a contact insecticide and as a stomach poison; its vapour pressure is sufficiently high for it to exert a fumigant action in closed spaces. It exhibits some residual toxicity but less than that of D.D.T.; Schrader<sup>28</sup> reports lethal deposits 6 to 8 days after application



on leaves and 6 to 8 weeks on bark surfaces. There is some evidence of absorption by the plant, and insects feeding on lower leaf surfaces may be killed by treatment only of the upper surface; it has however not yet been firmly established that fumigant action plays no part in this phenomenon. While there may be thus some transmission of the poison within the plant it appears certain that no extensive translocation takes place. The toxic action of Parathion on insects appears to be interference with the choline-esterase system<sup>29</sup> but other physiological reactions may also be involved.

The number of insect species reported to be killed by Parathion is very large<sup>31</sup> and already representatives of Lepidoptera, Coleoptera, Hemiptera, Diptera, Thysanura and Acarini are numbered among them. In many cases this work has so far involved only bench tests and it is as yet impossible to state against which pests it will eventually prove to give economic control in the field. Field tests have shown it to be a valuable aphicide, and to control certain caterpillars; it is reported to control red spider adults and eggs but the concentration needed to kill the latter is relatively high; against scale insects the results are still confusing and it would appear that in regions of high temperatures the control obtained may be insufficient, possibly because the residual action is curtailed by volatilization of the deposit.

Although since Schrader's initial work there has been sufficient investigation to show that Parathion is a powerful insecticide with a scope wider than that of hexa ethyl tetraphosphate, much research is still necessary into the toxic hazards of using this material. As the mode of toxic action appears to be interference of the choline-esterase system, the poison is not specific to insects but is also dangerous to mammals. Whereas hexa ethyl tetraphosphate (and tetra ethyl pyrophosphate) are quickly hydrolysed in the atmosphere, Parathion leaves a relatively stable deposit. Thus, apart from hazards involved in manufacture and application, which can be minimized by proper precautions, there is also the danger of acute and chronic poisoning resulting from ingestion of treated food. Lehman<sup>32</sup> reports that the median lethal dose by ingestion of Parathion is only 3.5 mg/Kg. (D.D.T. 250 mg/Kg.), while the estimated amounts dangerous to Man by dermal application are 0.6 mg. for a single application and 0.3 mg. for repeated exposure.



There is thus already evidence to confirm the desirability of careful study on the toxicity of Parathion and the precautions to be adopted before it is used on a wide scale.

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## CHAPTER XI

### SOIL INSECTICIDES AND AMENDMENTS

THE subterranean parts of plants are just as vulnerable to pest attack as are the aerial portions, for there are many injurious species of insects which pass part or the whole of their life cycle in the soil, feeding on or boring into the root tissue. Quite apart from insects, there is also a complex of soil organisms, of which nematode worms, fungi and protozoa are examples, which are inimical to plant growth and must be controlled to secure a healthy crop with high yields. Many of the chemicals which are applied to the soil for the control of one specific pest also reduce the activity of other members of the complex and in these cases it is customary to term them "soil amendments" rather than soil insecticides.

Although many economic crops are subject to attack by soil insects such as wireworms and cockchafers, which may cause very considerable damage, it seems probable that the greatest losses result from a condition known as "soil sickness" which is most prevalent in areas of intensive cultivation, especially where the same crop is grown year after year. One of the most potent factors in soil sickness is the presence of injurious nematode worms and a method for controlling these is one of the pressing agricultural problems of to-day.

The control of harmful soil organisms may be approached in a number of ways. Certain cultural operations are of benefit; thus ploughing may destroy the habitat of the pest which is then exposed to desiccation and its natural enemies; crop rotation may be designed to starve out the pest by ensuring a lack of suitable host plants; and in a few cases advantage may be taken of a naturally resistant variety to secure root stocks which are more or less immune to attack as, for example, the use of American vine stock to resist the phylloxera pest. In general, however, cultural methods are, at the best, palliatives and more direct treatment, such as that by heat or chemicals, is necessary to secure full control of harmful soil organisms. In this more drastic treatment it is necessary to strike a balance between the elimination of



the harmful organisms and the preservation of those which are beneficial; thus only partial sterilization of the soil is required and not the destruction of all organisms.

Partial sterilization of soil may be accomplished by heating to 97° C. and maintaining it at that temperature for one hour. While this method can be used for small plots, such as glasshouses where steam is the agent usually employed, it is nevertheless a costly operation and it has so far proved impossible to design a machine or a system so that this method can be used economically in the treatment of large acreages. It should be noted that heat treatment acts as a true soil amendment. Crops planted after its application show an increase in growth and yield which cannot be accounted for by the simple elimination of insect and fungal pests; for this reason, many growers practise steam sterilization of glasshouse soil, not primarily for the elimination of a particular pest, but in order to profit from the increased fertility of the soil.

For the practical and economic control of harmful soil pests in the field, the farmer must resort to the use of chemicals. Soil insecticides must satisfy a number of requirements to be of practical value and two of the most important are, firstly, that it should be cheap and economical in use, and secondly, that it should be capable of easy dispersal through the soil. The question of cost is paramount in view of the extensive areas which must be treated and there are a number of chemicals which act in a satisfactory manner but their cost of application is not warranted by the increased yield in crop obtained. Penetration of the insecticide throughout the soil is necessary to ensure contact with the pest and for this reason the majority of chemicals used are volatile and although they may be applied in the liquid or solid form they are really acting as fumigants; penetration of certain other insecticides is accomplished by using them in water solutions and emulsions, while in other cases the necessity of complete dispersion is avoided by using them in conjunction with an attractive bait. The material used must also have no deleterious effects on the plants themselves and although few soil insecticides or amendments are non-phytotoxic if applied directly to the living plant, the majority of them can be applied when the land is fallow and by allowing a suitable interval between treatment and seeding or planting out the material is dissipated and



harmful effects to germination or plants avoided. Although some hundreds of chemicals have been tested for suitability in the control of injurious soil pests, not one has yet been discovered which possesses all the properties which are desirable but the recent development of a dichloropropene-dichloropropane mixture as a soil amendment would appear to be a closer approach to the ideal material than has been suggested hitherto.

In the space at our disposal it is impossible to give more than a brief outline of this subject on which much active research is now in progress. An arbitrary selection has been made of some of the better-known soil insecticides and some of the new materials which show promise but the specialist is referred to the monograph by Gough<sup>1</sup> wherein reports on more than 250 chemicals are reviewed.

### Carbon disulphide

Carbon disulphide,  $\text{CS}_2$ , is a colourless liquid when pure but the commercial product is sometimes a pale yellow colour. Its specific gravity at  $15^\circ \text{C}$ . is 1.27, the boiling point  $46^\circ \text{C}$ . and it is inflammable with a flash point of  $-25^\circ \text{C}$ .; it possesses a distinctive unpleasant odour. According to Gough<sup>1</sup> carbon disulphide is the most widely used of all soil insecticides.

The insecticidal properties of carbon disulphide appear to have been discovered in the middle of the nineteenth century and its first application on a wide scale took place some fifty years later when it was used for the control of the vine phylloxera which was then sweeping through the vineyards of France. Since that time, it has been used for the control of a number of pests and although far from ideal in its cost and ease of application, it has, nevertheless, retained considerable popularity.

A number of methods of applying carbon disulphide to the soil have been developed, the most common of which is injection using an injector "gun"; the gun, in principle, consists of a hand pump delivering known volumes of liquid carbon disulphide through a spiked pipe which pierces the soil to the required depth. In France, a mechanical applicator was developed for large scale application by adapting a plough in such manner that the land wheels operated a pump which



allowed controlled quantities of the carbon disulphide to flow into the furrow as the machine proceeded.

The present trend of development is towards the use of carbon disulphide emulsions and water miscible preparations which can be watered into the soil. Flemming and Baker<sup>2</sup> investigating the formulation of these preparations reported unsatisfactory results when using commercial soaps which varied in quality from batch to batch; Lipp<sup>3</sup> developed a relatively stable emulsion by formulating with a sodium oleate-resin soap which was satisfactory except at low temperatures. A number of water-miscible carbon disulphide preparations have also been developed by the same workers and these were made up with an alcoholic soap solution incorporating blown castor oil and potassium hydroxide; they were miscible with water in all proportions and could be applied to the soil to give any desired dose of carbon disulphide per unit area.

Higgins and Pollard<sup>4</sup> studied the distribution of carbon disulphide after injection into the soil and found that the highest concentration persisted around the immediate site of application and that there was a rapid fall in concentration in the upper soil layers and a similar, though less rapid, fall below the injection point. Flemming and Baker<sup>2</sup> also investigated this aspect and they concluded that the distribution of the gas is cone-shaped, with the apex seated at the point of injection. The penetration of the gas is more successful in fairly dry, sandy or humus-soils and is least effective in moist and heavy clay soils.

Carbon disulphide has given satisfactory control of crickets, termites, the subterranean colonies of woolly aphis, cockchafer, wireworms and many other soil-inhabiting insects which cause economic damage. It is phytotoxic but when used as a constituent of an emulsion, plants have shown little or no injury.<sup>2</sup> The chief limitations to its use are its cost, unpleasantness in handling and the possible fire or explosion risk. Gough<sup>1</sup> summarized the results of treatment with carbon disulphide as follows: "The recommended rates of application vary between 20 and 400 grams per square metre. Quite a high proportion of successful results have been recorded between 20 and 40 grams per square metre for insects other than coleopterous larvae. For these, rates in the region of 300 grams per square metre appear to be necessary, though some workers have obtained high kills with lesser amounts. Emulsions watered on to



the soil so that 50–100 grams per square metre of carbon disulphide is applied appear to have given good results in the control of most soil pests, and they thus appear to be rather more economical in material than injections of the pure substance.”

### Calcium cyanide

Calcium cyanide,  $\text{CaCN}_2$ , is a white crystalline powder which decomposes in the presence of moisture liberating hydrogen cyanide. As a soil insecticide, it has been applied in a number of ways, both as an aqueous solution and as a powder; it may be applied to the base of plants or to holes in the ground, drilled into the earth with a seed drill, or broadcast by hand or a suitable distributing machine and then ploughed or harrowed into the soil. In each case, it is the hydrogen cyanide liberated which produces the lethal effect.

Effective control has been recorded, at application rates varying from 12 to 300 pounds per acre, against many species of insect, of which crickets, Colorado beetle and raspberry crown borer (*Pennisetia marginata*) are examples. On the other hand, there is an equally lengthy list of insects against which it has proved ineffective. Both Horsfall<sup>5</sup> and Campbell<sup>6</sup> have reported high mortality rates in wireworms but, in general, this chemical has not proved very effective as a soil insecticide and caution should be used in its use as the dosages required may cause injury to fruit trees, vegetables and flowers. It can be used in conjunction with suitable baits such as potato, maize, flour, etc., when satisfactory control of wireworms has been recorded at application rates varying from 100 to 200 pounds per acre.

At one time, it was considered that calcium cyanide was efficient as an eelworm (nematode) control for experiments showed treated areas to have a stronger plant growth and higher yields than comparative untreated plots. It is now generally considered, however, that this effect is not the result of eelworm kill but a fertilizing effect caused by the additional nitrogen supplied by the chemical.

### Chloropicrin

The properties of chloropicrin,  $\text{CCl}_3\text{NO}_2$ , are described in the chapter on fumigation. This liquid, which volatilizes slowly at the usual soil



temperatures, is a highly efficient soil fumigant by reason of the association of a nitrogroup with chlorine and, furthermore, acts as a soil amendment, for it possesses not only some fungicidal and bactericidal properties, but treatment with it brings about increased fertility in the soil.

Chloropicrin can be applied directly to the soil as an undiluted liquid, or it may be prepared as a water emulsion, using soap as an emulsifier and watered into the soil; still another method of application is to absorb the toxicant on inert dusts such as kieselguhr and to dig this preparation into the ground. It has not been used on a wide scale for treatment of large areas because of its unpleasant and dangerous properties, but in experimental work complete control over some wireworms (*Limonius feruginosus* and *Corymbites latus*) has been reported at dosages corresponding to 540 pounds per acre when the liquid was introduced into holes of 4 to 10 inches depth. Donohoe<sup>7</sup> has also reported successful pot experiments demonstrating control over the Japanese beetle at dosages of 3.5 mil. per square foot of surface, but a practical means of applying the material safely on a field scale still remains to be discovered. Chloropicrin is highly toxic to plants and cannot be used in standing crops.

It has now been known for a number of years that chloropicrin acts as a soil amendment and can be used successfully to combat "soil sickness"; it is, furthermore, one of the few soil fumigants which can be used to control harmful nematode worms. While the greatest benefit to the plant from soil disinfestation is the elimination of harmful organisms, the increased "fertility" effect following some treatments is also of considerable importance. Chloropicrin is one of the soil amendments producing growth stimulus and the mechanism has been studied by Tam<sup>8</sup> using pineapple as the test plant. The process is a complex one possibly involving the suppression of protozoa inimical to beneficial bacteria and also the disturbance of the balance between the species of bacteria themselves; thus Tam has related the increase in top growth of pineapples following chloropicrin soil treatment to the suppression of nitrification of ammonium salts, whereby the plant, unable to use nitrate nitrogen, takes in ammonium nitrogen which has been shown to stimulate early rapid growth.<sup>7</sup>



In spite of the high efficiency of chloropicrin as a soil amendment, its unpleasant and dangerous nature has greatly limited its use and it seems improbable that it will ever be developed for application on a wide scale.

### **Dichloropropene-dichloropropane mixture ("DD")**

"DD" has proved to be a powerful nematocide and insecticide and its relatively low cost permits its use as an economic soil fumigant. It is applied by injecting directly into the soil at dosages varying from 200 to 600 pounds per acre, according to the species of pest and the nature of the soil, but the most usual rate is 200–300 pounds; where small areas are involved, hand injector guns may be used or, more simply, known quantities of the fluid may be poured into holes prepared in the ground; for large acreages, mechanical applicators have been developed which are power-driven and inject known amounts of "DD" as the machine travels over the ground. It has been established that at normal doses in average soil the diffusion of the fumigant from a point of injection 8 inches deep is approximately 9 inches in a lateral direction, 18 inches downward, and to the surface in an upward direction. In practice, therefore, injection points are made 12 inches apart to ensure complete penetration throughout the top soil layer. The fumigant is phytotoxic and cannot be used in standing crops but is applied in the tilled fallow soil a few weeks before seeding or planting out. Although "DD" irritates the skin if left in contact with it, simple precautions such as washing any splashes off with soap and water counteract any ill effects and it is unnecessary to use only skilled operators during application.

The insecticidal and nematocidal properties of "DD" were first discovered by Carter<sup>9</sup> during his investigations into the control of a complex consisting of nematodes, Asiatic beetle (*Anomala orientalis*) larvae and pythiaceus fungi which were seriously attacking pineapple in Hawaii. He obtained striking results at the initial rate of application of 150 pounds per acre and followed these trials with others on vegetable crops which demonstrated the effectiveness of "DD" as a nematocide against the root knot eelworm (*Heterodera marioni*) attacking vegetable crops. Carter's reports aroused great interest in the United States



where the necessity for increased food production in wartime was stimulating the search for an efficient nematocide and field trials were set up in many State Agricultural Stations to investigate the effectiveness of "DD" under varying conditions. The combined results were very favourable and the 1944 report of the Administrator of Agricultural Research, U.S. Department of Agriculture,<sup>10</sup> announced that in sandy loam soil the fumigant would give 99–100 per cent. control of root knot nematode when applied at 500 pounds to the acre and that the dosage could be reduced to 200 pounds per acre without much loss in efficiency. Since 1944, "DD" has been subject to much investigation and has taken its place as the most promising soil amendment which is capable of economic application.

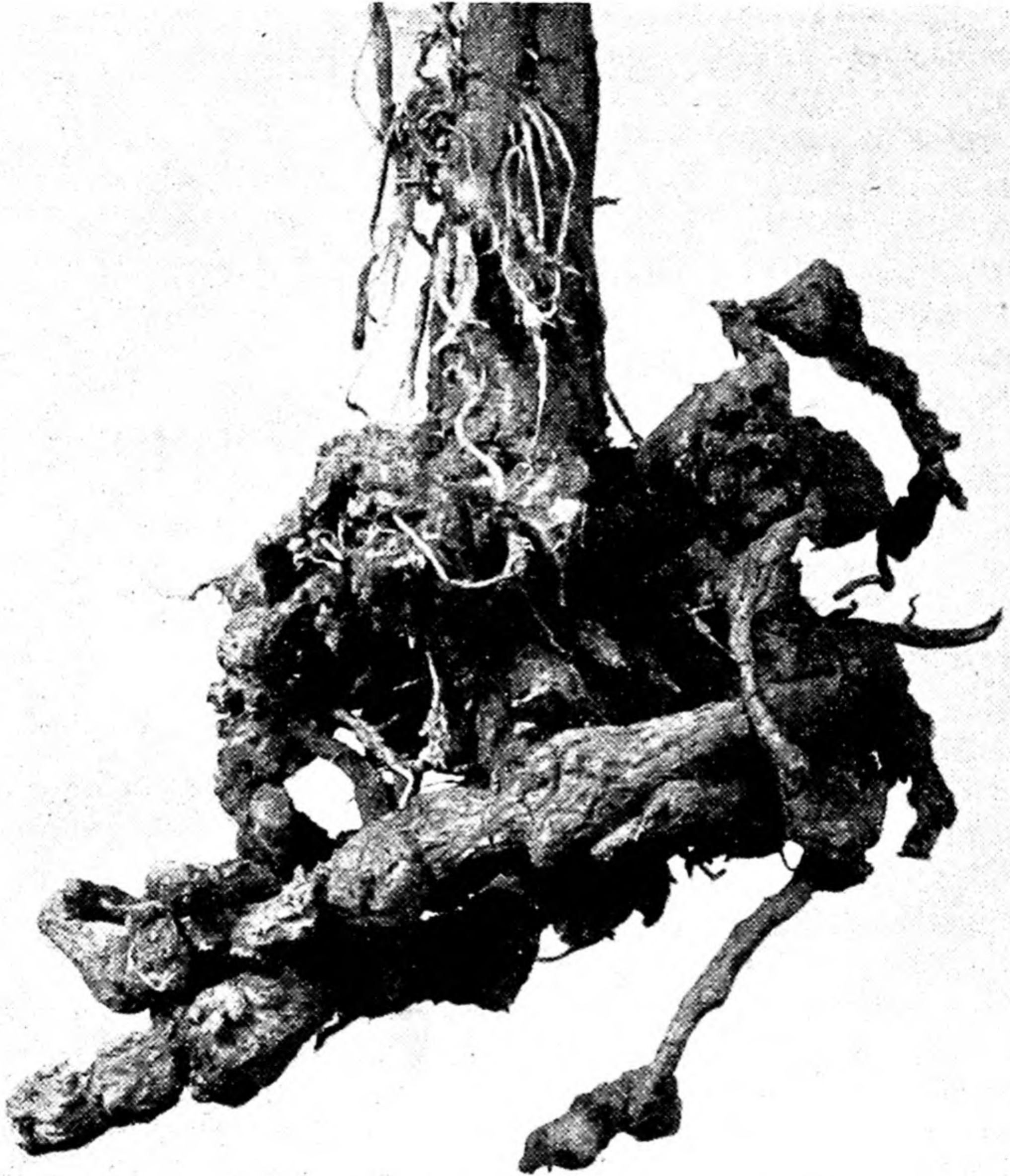
Up to the present time, the emphasis in scientific investigation has been placed chiefly on its nematocidal value and almost the whole of the quantities available for practical use (amounting to some thousands of tons per annum) are absorbed primarily for eelworm control. However, sufficient studies into its insecticidal value have been made to indicate that it can be used against the majority of soil inhabiting insects.

Parris<sup>11</sup> confirmed the results of Carter and concluded that there was no advantage to be gained from using the more expensive redistilled mixture consisting only of dichloropropene and dichloropropane as compared with the crude products which contain in addition, the trichlorides and tetrachlorides of 3-carbon atom compounds. Subsequent investigation has indicated that the components of the crude mixture have some synergistic effect for the combined control appears to be greater than would be expected from the summation of the effects of each component assessed separately. Parris also concluded that the action of "DD" is not influenced by low soil temperatures (38–40° F.) but that in such conditions a longer interval between treatment and sowing is necessary to allow dissipation of the phytotoxic elements.

Although it has now been established that "DD" will control root knot nematode under conditions met in the United States and workers<sup>12,13</sup> in the United Kingdom and other areas are beginning to obtain the same results, further investigation is required to ascertain the correct dosages necessary to control the more resistant potato eelworm which



is a scourge in Great Britain and in parts of Western Europe. In America, Chitwood and Buhrer<sup>14</sup> obtained a 79–99 per cent. reduction



**Fig. 24.**—Tomato root showing damage by root knot eelworm. *A Shell Photograph.*

in the potato eelworm (*Heterodera rostochiesis*) population with phenomenal crop increases on infested land which often resulted in double or triple crop yields; similar experiments are now being carried



on in Great Britain and other areas but the results have not yet been published.

The records of large-scale field trials in which "DD" has been used solely as an insecticide are as yet very few but Lange<sup>15</sup> records wireworm control in irrigated land under intensive cultivation when using a dosage of 400 pounds per acre; reference has already been made to the control of the Asiatic beetle attacking pineapple.<sup>9</sup> Tam<sup>8</sup> showed that "DD", like chloropicrin, suppresses nitrification in the soil for a period after application and during this time plants are able to use ammonium nitrogen with a consequent increase in growth and yield; Lange<sup>15</sup> similarly observed that simultaneous applications of "DD" and ammonia gave very high yields in the subsequent crop of lettuce. Advantage has been taken of this phenomenon in California, where the injection of anhydrous ammonia into the soil for nitrogenous fertilization has been developed, to apply "DD" and ammonia simultaneously from the same mechanical applicator.

It is still too early to assess the full value of "DD" as a soil amendment but those investigations which have already been completed, coupled with the extensive commercial application which has developed in the United States and Hawaii indicate that it will find many and varied uses in soil treatment.

### Dichloroethyl ether

Dichloroethyl ether,  $C_4H_8Cl_2O$ , exists in two forms, of which one,  $\beta$ ,  $\beta$ -dichlorodiethyl ether ( $CH_2Cl.CH_2O.CH_2.CH_2Cl$ ) is a liquid with a boiling point of  $178^\circ C$ . while the other,  $\alpha$ ,  $\beta$ -dichlorodiethyl ether ( $CH_2Cl.CHCl.O.CH_2CH_3$ ) boils at  $143^\circ C$ . Of the two forms, the  $\beta$   $\beta'$ -compound has been used chiefly as a soil fumigant as its higher boiling point permits the fumigating action to proceed over a longer period. It has usually been applied to the soil by means of emulsions or aqueous solutions.

Eddy<sup>16</sup> has reported that an aqueous dichloroethyl ether emulsion was successful in controlling the wireworm (*Horistonotus uhleri*) without damage to cotton and maize, while preliminary pot experiments by Campbell and Stone<sup>17</sup> demonstrated that a solution of 5 mil. of  $\beta$   $\beta'$ -dichloroethyl ether in 1 gallon (U.S.) of water would give a 100 per



cent. kill of the wireworm (*Limonius culifornicus*) at a depth of 8 inches when the dosage corresponds to 1 gallon per cubic foot of soil; the penetration of the solution falls off rapidly below depths of 8 inches and at 12 inches only, a 33 per cent. kill was recorded. They followed these laboratory experiments by a field trial, using a solution at the same strength on planted beans, at the rate of 1 gallon per 15 feet of row and reported a 94.7 per cent. control of wireworm.

Dichloroethyl ether has been reported to give control over woolly aphis, webworm (*Crambus* sp.) and a considerable variety of other soil insect pests at varying rates of application. The extent of phytotoxic action appears to vary with different plants and whereas cereals do not appear to be harmed, damage has been reported to tobacco<sup>18</sup> and tomato.<sup>19</sup> Dichloroethyl ether has also been tried in conjunction with other soil insecticides, such as ethylene dichloride emulsion for the control of pine root weevil (*Hylobius radius*) and methyl bromide emulsion against alfalfa weevil and in each case promising results have been reported.

Dichloroethyl ether has not yet been fully developed as a soil insecticide and the results of large-scale field trials must be awaited before a full assessment of its possibilities can be made.

## MISCELLANEOUS SOIL INSECTICIDES

**Naphthalene**,  $C_{10}H_8$ , is a white crystalline solid which is insoluble in water but possesses a relatively high volatility and rapidly saturates with its vapour the air in a confined space. It has been used as a soil fumigant against wireworms, leatherjackets, cockchafer larvae, and cutworms by incorporation into the soil at rates varying from 300 to 800 pounds per acre but the results in practice have proved inconsistent and Gough<sup>1</sup> suggests that the soil temperature may be an important factor and that owing to its repellent properties insects may temporarily disappear without true control being obtained.

**Para-dichlorobenzene** is a white crystalline solid and is highly volatile at normal air and soil temperature. In experimental trials some successful results have been obtained against the clover root borer, the Japanese



beetle and a number of root aphids and borers. It has not been successful for the control of wireworms and its high cost coupled with the large dosage (300–1,000 pounds per acre) necessary to give control places this chemical outside the range of practical soil fumigants.

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## CHAPTER XII

### PYRETHRUM

ACCOUNTS of the early history of the use of insect powder do not agree, but the property of various species of pyrethrum flowers in killing insects was known in Eastern Europe well over a century ago. In 1851,<sup>1</sup> Koch stated that the celebrated Persian insect powder consisted of powdered flowers of *Chrysanthemum roseum* and *Chrysanthemum carneum*. It is said<sup>2</sup> that early in the nineteenth century an Armenian merchant travelling in the Caucasus discovered that insect powder consisted of these flowers, developed manufacture, and began exporting to Western Europe in about 1820. The discovery and early commercial development of powders based on *Chrysanthemum cinerariaefolium*—from which the Dalmatian insect powder was prepared—is also unknown. De Visiani in 1854 mentioned the use of this plant as an insecticide, but the inhabitants, to keep production to themselves, baked seeds supplied for cultivation elsewhere to prevent germination<sup>1</sup>: in this account the term pyrethrum is applied to *Chrysanthemum cinerariaefolium* since, although other pyrethrin-containing plants—notably *Chrysanthemum roseum* and *Chrysanthemum carneum*—do exist, they are not now of commercial interest.

Importation of flowers from Europe (Dalmatia) to the United States—now by far the largest peacetime consumer—began about 1885. Pyrethrum was introduced experimentally into Japan in 1881.<sup>3</sup> Serious cultivation began in 1886 and extended until, when the supply from Europe was cut off during the 1914–18 war, Japan became the principal world source. In 1925,<sup>4</sup> the Plant Pathological Laboratory of the Ministry of Agriculture under the direction of Sir John Fryer investigated the possibility of growing pyrethrum flowers in this country.

Although flowers with a satisfactory pyrethrin content could be obtained, the cost of harvesting made the project impracticable commercially. However, these experiments and the pioneer work of Dr. Tattersfield and co-workers at Rothamsted played a considerable part in the



development of the pyrethrum industry in Kenya. Experiments undertaken in Kenya in 1928 showed that in the cooler districts at elevations of about 5,000 to 8,000 feet, pyrethrum was a suitable crop. The area under cultivation increased until in 1934 an exportable surplus of flowers was produced and in 1939 Kenya superseded Japan as the world's largest producer of pyrethrum. The Kenya settlers enforced the registration of all pyrethrum growers and prohibited export except through the Kenya Farmers' Association.<sup>5</sup> The rapid growth of the Kenya industry at the expense of the Japanese is due to the superior quality and uniformity of the Kenya flowers.<sup>6</sup> Thus (a) although of the same species, the Kenya flowers are richer in active ingredients than the Japanese flowers (1.3 per cent. against 0.9 per cent. by weight are average figures). (b) The Kenya climate allows almost a year-long harvest, and hand picking ensures that only mature flowers are collected. Tattersfield and co-workers showed that there is a quantitative development of active principle in the flowers from the small-bud stage up to maturity. In Japan only one crop per year is obtained. (c) Kenya flowers are dried in especially constructed driers under standard conditions so that the colour and moisture content do not vary greatly, whereas Japanese flowers are spread like hay to dry in the sun. If there is rain, discoloration, fermentation and loss of pyrethrin content can take place. The usual moisture content of Kenya flowers is 5–7 per cent., but in Japanese flowers it is about 15 per cent.<sup>7</sup>

The dried Kenya flowers are compressed into 4-cwt. bales.<sup>8</sup> For manufacturing, these bales are broken up and the flowers ground in various types of mills—the degree of fineness depending upon the use for which the product is intended—avoiding overheating which might damage the active principles. Tattersfield and Martin<sup>9</sup> found that pyrethrum powders and the dusts prepared by incorporating extracts of pyrethrum in inert materials deteriorated on exposure to light and air. The impregnated dusts were particularly susceptible but the loss of activity was retarded by the addition of antioxidants. The degree of fineness of the powder affects insecticidal properties; for instance, Smith<sup>10</sup> found that the time required for pyrethrum powder to paralyse mosquito larvae decreased markedly as the particle size of the powder decreased. The finer powders deteriorated more rapidly but were



stabilized by the addition of tannic acid or pigments such as titanium dioxide possessing a high index of reflection of light waves. In some instances, it has been found that pyrethrum powders were less effective than impregnated dusts.

Although kerosene extracts of pyrethrum were recommended for controlling insects on plants fifty years ago,<sup>11</sup> it was not until after the Great War that such products were offered commercially. It is of some interest to recall that Terry<sup>12</sup> was granted a U.S. patent as late as 1926 protecting the manufacture of a liquid household insecticide consisting of a solution in a mineral oil such as kerosene of the volatile active principles of pyrethrum. In the litigation which followed, the patent was held invalid and it was proved that such products had been used in the U.S. Navy during the war. It is surprising, in view of the diversity of pyrethrum extracts now available, that up to about 1920 the material was used almost invariably as a powder. When the first kerosene extracts were put on the market, manufacturers based their strength on the weight of flowers per gallon basis. In 1924 the insecticidal properties of pyrethrum flowers were shown to be due to two esters—pyrethrin I and pyrethrin II.

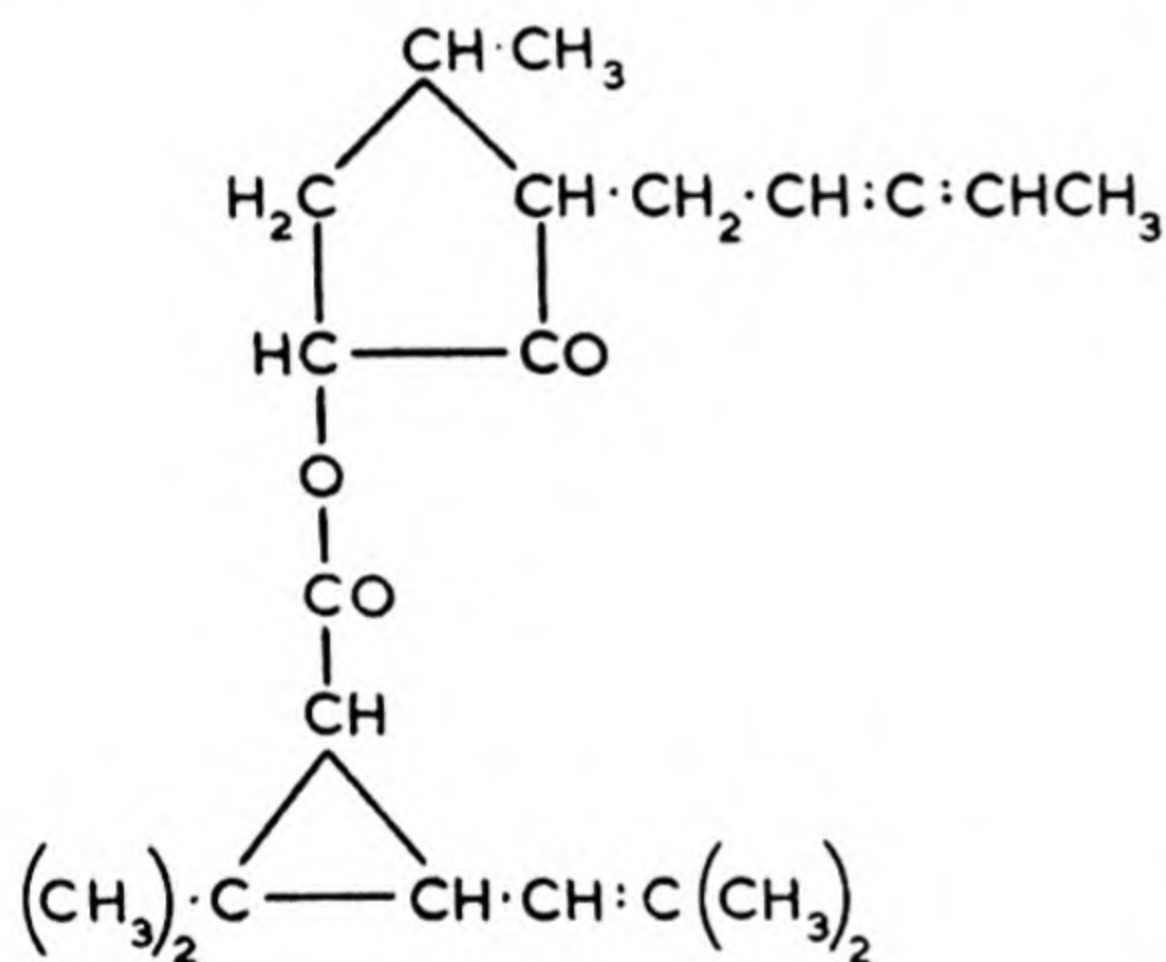
It was not until about 1929 that the methods evolved for determining the pyrethrin content of flowers revealed that flowers were then on the market with pyrethrin contents varying between 0.4 and 1.2 per cent.<sup>11</sup>

Mineral extracts of pyrethrum can be prepared by direct treatment of the ground flowers with oil and the removal of the oil retained by the flowers by centrifuge, hydraulic press or by means of an oil expeller. Gnadinger<sup>11</sup> held, however, that direct extraction is not, in general, commercially practicable because the flowers absorb large quantities of extract. But the pyrethrins are readily soluble in organic solvents of which Gnadinger considered ethylene dichloride a satisfactory initial solvent. The flowers are extracted, the ethylene dichloride removed by distillation and the resulting oleoresin extracted with kerosene or other carrier. It has been claimed<sup>13</sup> that insecticidal products can be prepared by subjecting the flowers or extracts to short-path high-vacuum distillation at an elevated temperature. The pyrethrins themselves are viscous liquids (non-steam volatile) which cannot be satisfactorily purified by distillation *in vacuo* and from the molecular structure this lack



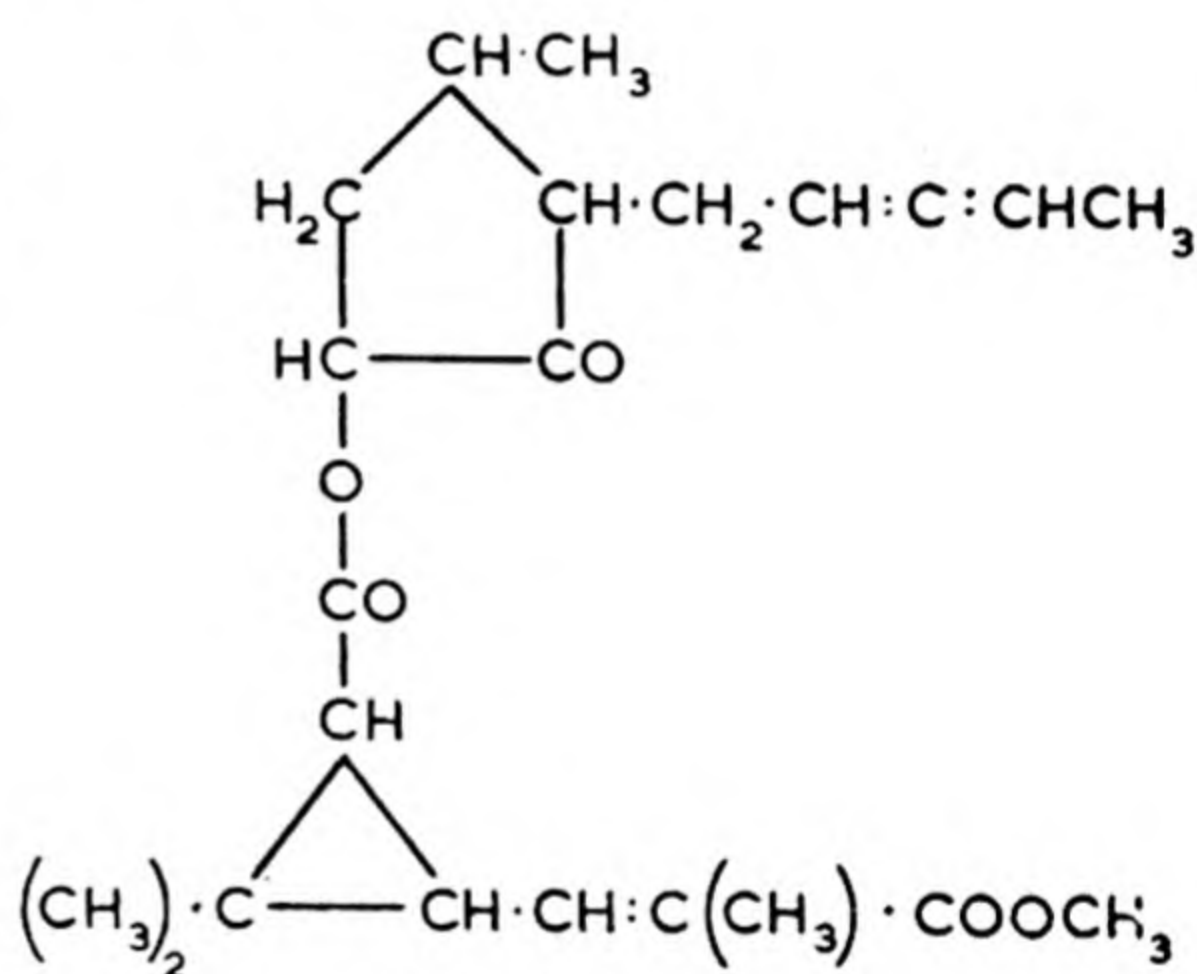
of stability is not surprising. At the same time, properly-prepared extracts retain their toxicity substantially unimpaired for years. Pyrethrum products should be kept in a cool storage and liquid extracts especially should be kept in the dark and out of contact with lead, brass and zinc. The question of the deterioration of pyrethrum extracts on exposure to air has been reviewed recently by Trusler<sup>14</sup> who confirmed the beneficial effect of the addition of suitable antioxidants.

It is unnecessary to discuss the various attempts to isolate the active constituents (this early work has been fully reviewed elsewhere<sup>1,11</sup>) which preceded the classical work of Staudinger and Ruzicka. In 1924 a series of papers<sup>15</sup> appeared describing work carried out by these authors during the years 1910-16. They assigned structural formulae (I) and (II) respectively to pyrethrin I and pyrethrin II.



PYRETHRIN I  
(STAUDINGER AND RUZICKA 1924)

Fig. 25



PYRETHRIN II  
(STAUDINGER AND RUZICKA 1924)

Fig. 26

The work of LaForge and Haller<sup>16</sup> (1936) led to the replacement of the cyclopentanolone by the cyclopentenolone nucleus in the pyrethrolone fragment. Gillam and West<sup>17</sup> (1942) from a consideration of absorption spectra data showed that the pyrethrolone fragment contained two separate chromophoric systems (a) an  $\alpha\beta$  unsaturated carbonyl group in a five-atom ring environment; (b) a conjugated dienoid system in the side chain. This observation led to a search<sup>18</sup> for an



explanation for the anomalous chemical reactions of the pyrethrolone fragment of the pyrethrin molecules. Meanwhile, LaForge and Barthel<sup>19</sup> subjected pyrethrolone to an exhaustive examination to detect heterogeneity and succeeded in isolating no fewer than five semicarbazones combining a process of fractional distillation and acetylation before converting the fraction into semicarbazones. West<sup>20</sup> has isolated a sixth semicarbazone from the mixture. Summarizing the position as it stands to-day, the pyrethrins have been shown to consist of a mixture of dextrorotatory and racemic forms of four structurally different compounds (I), (Ia), (II) and (IIa) in which compounds (I) and (II) predominate.

Various chemical methods have been proposed for the determination of the pyrethrins. That generally used in commerce appears to be the Seil method and flowers are usually bought and sold on the basis of this test.

Assessments by different workers of the relative toxicity to insects of pyrethrins I and II have shown much variation. The latest work on this aspect is due to J. T. Martin.<sup>21</sup> The published results indicate that when dissolved in petroleum oils, the two compounds show an approximately equal effect, whereas, when suspended in aqueous media, pyrethrin II is considerably less toxic than pyrethrin I. In kerosene solution, pyrethrin II effects a quicker knockdown of flies than pyrethrin I.<sup>22</sup>

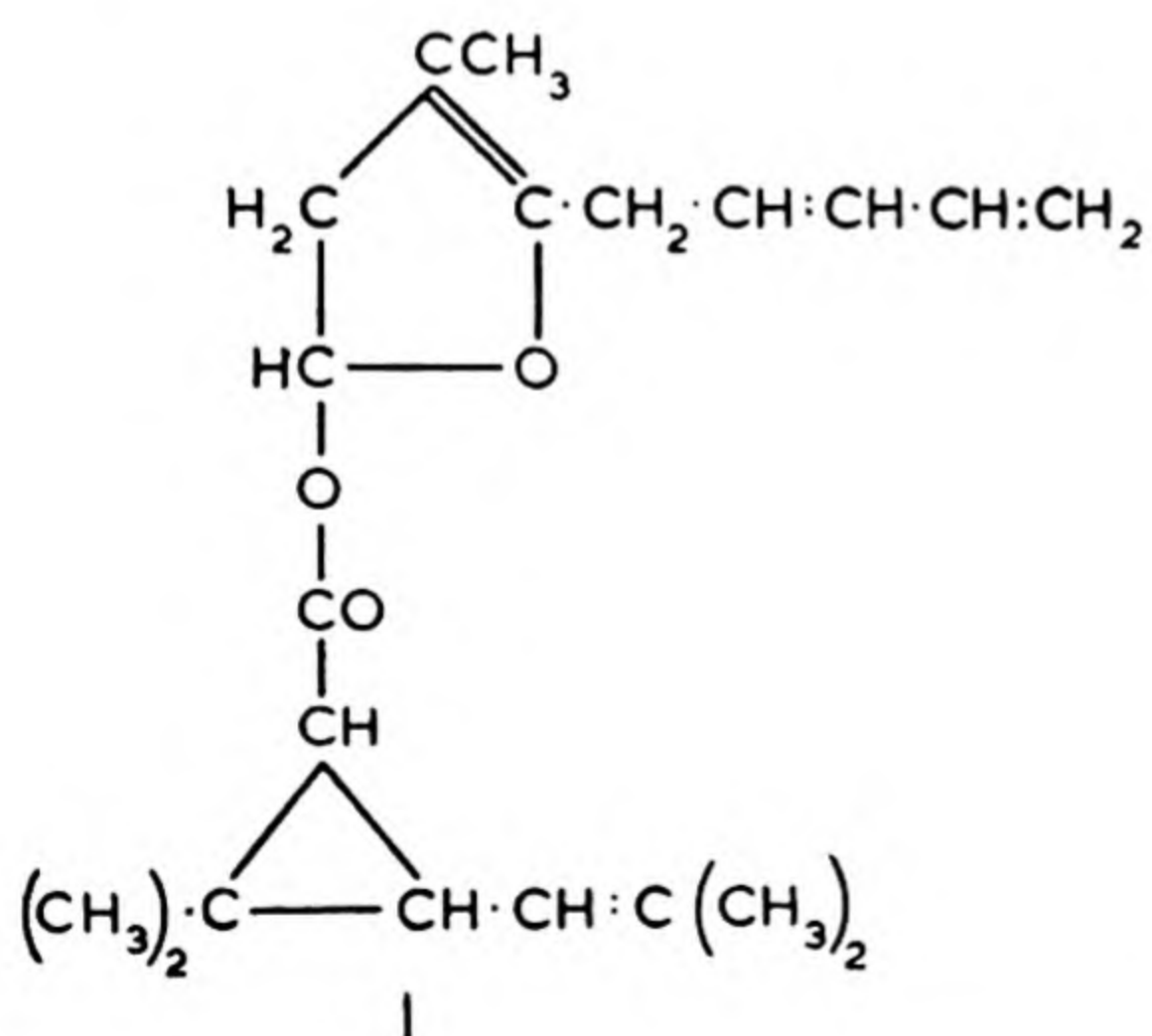


Fig. 27

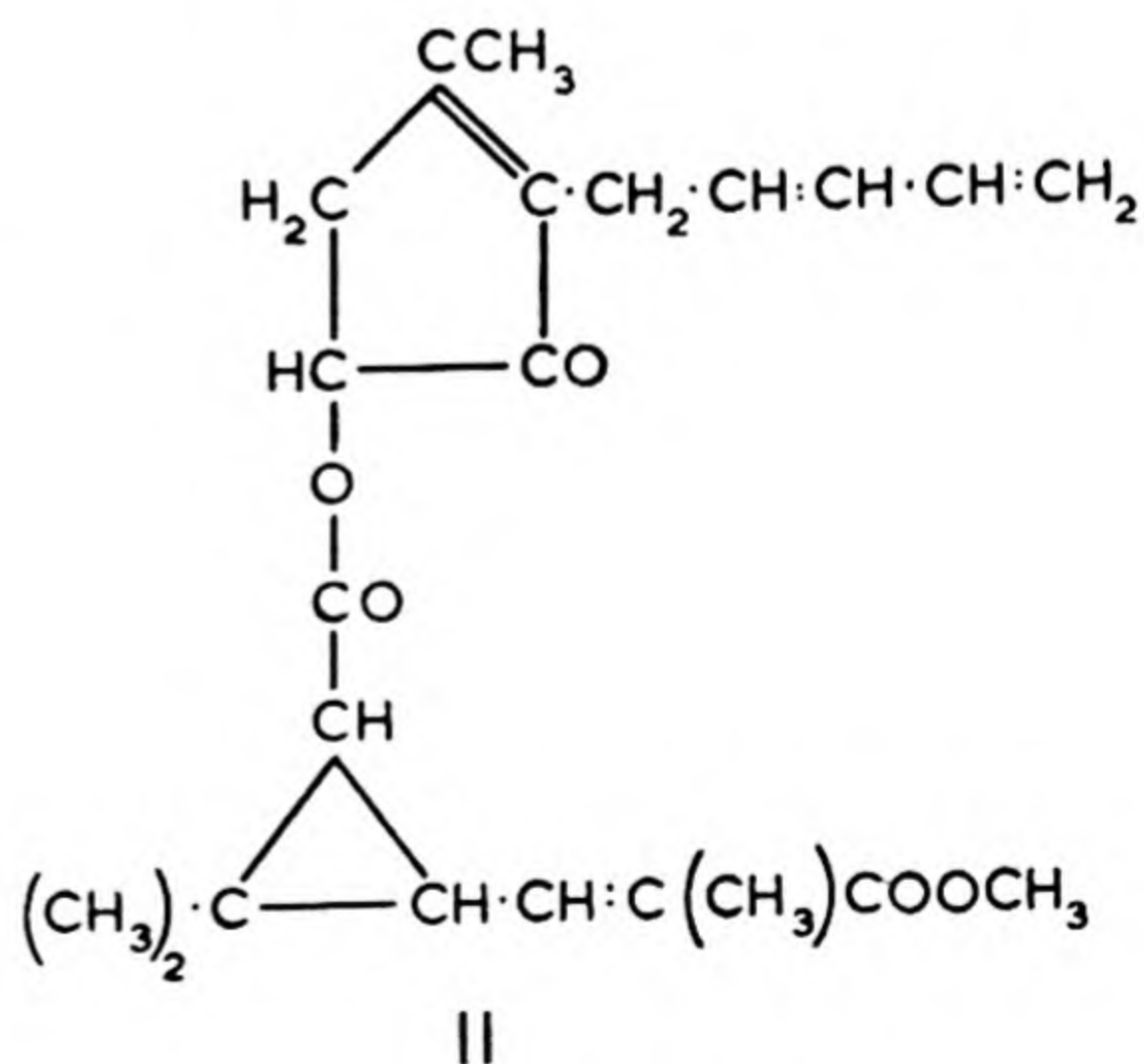
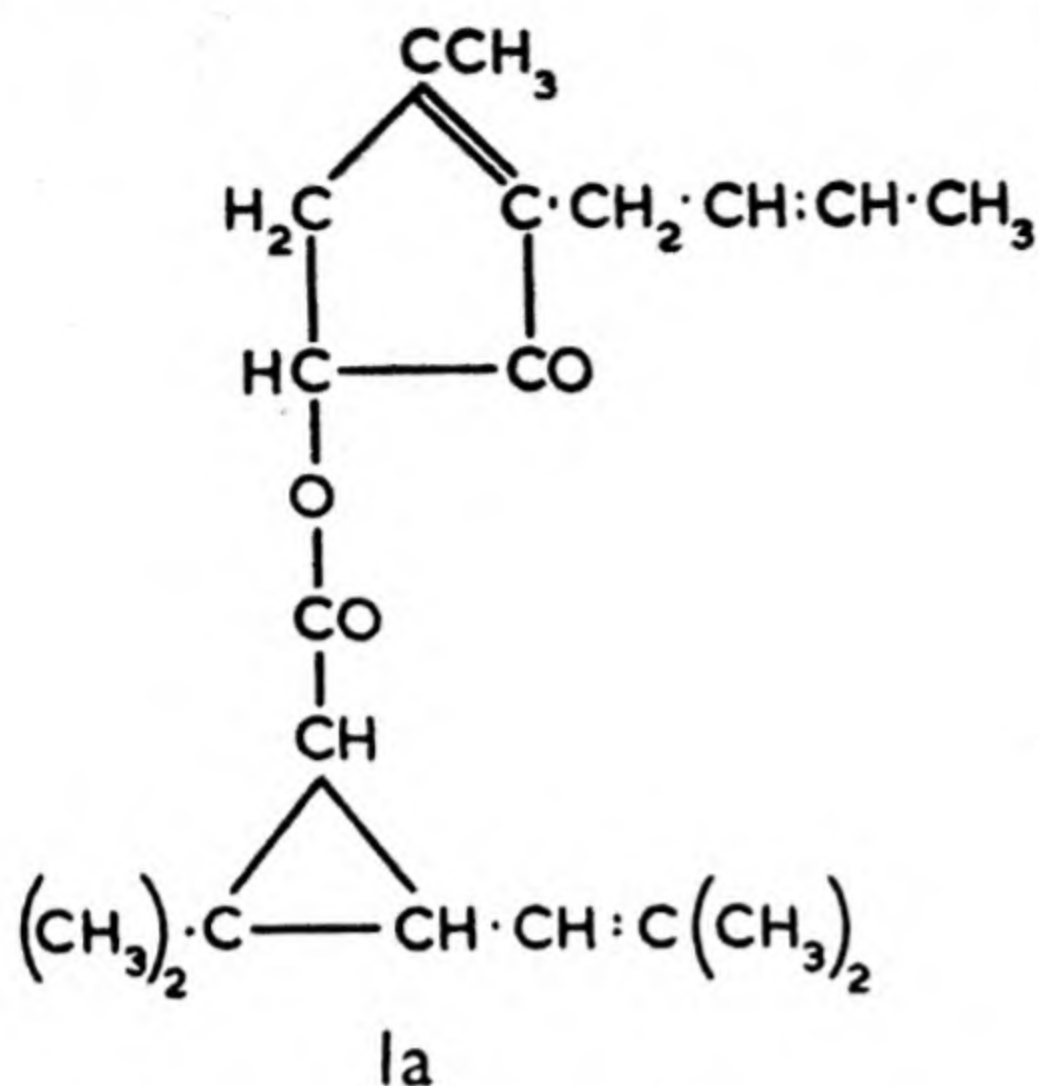
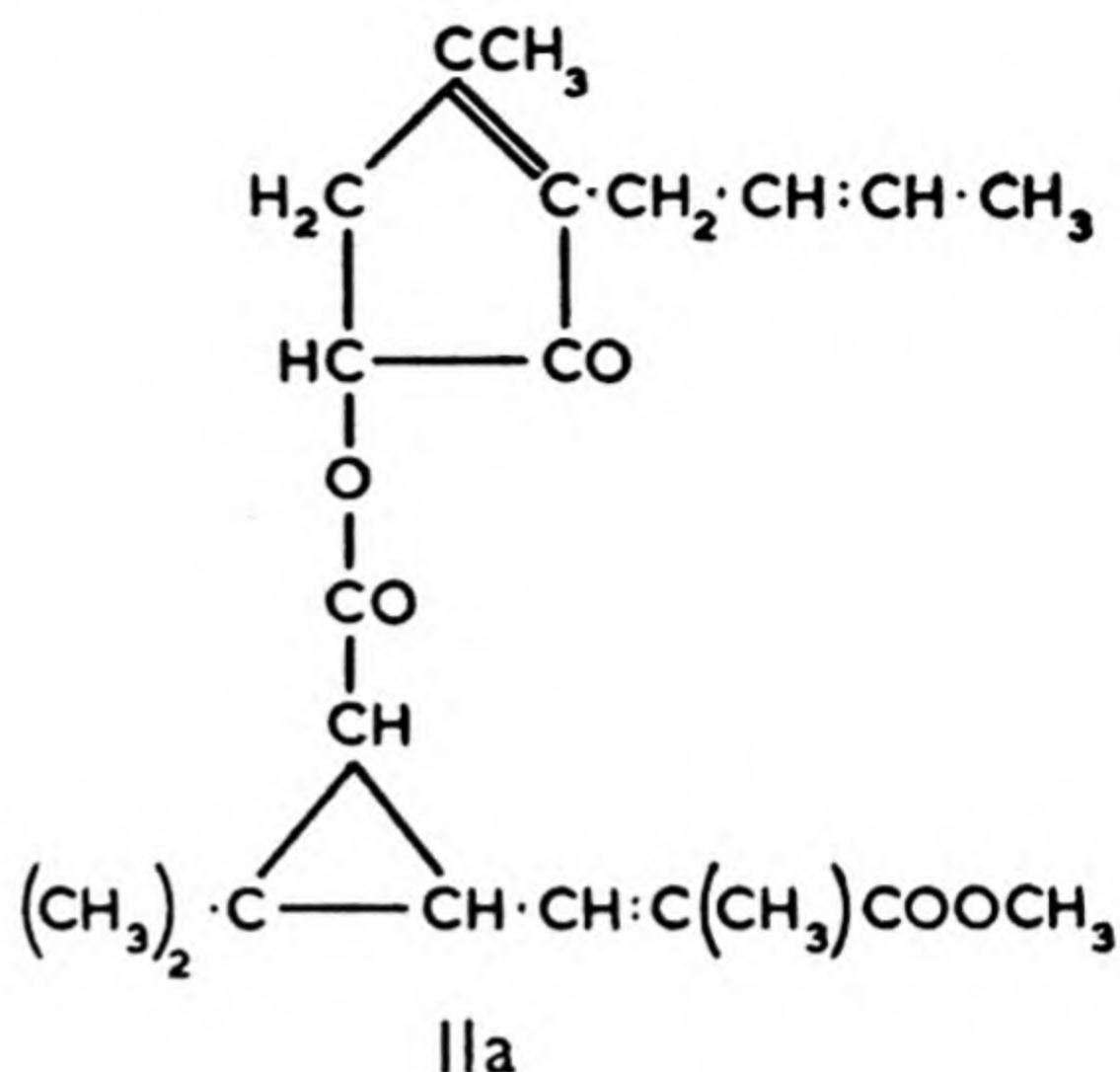


Fig. 28





**Fig. 29**



**Fig. 30**

The general method in use at present for the bioassay of pyrethrum sprays is that due to Peet and Grady. Flies are sprayed with the unknown solution of pyrethrins under specified conditions and the kill compared with that obtained with a standard kerosene solution of pyrethrins (Official Test Insecticide). Methods involving the exposure of insects to a film of pyrethrum insecticide have recently<sup>23</sup> been examined in this country by workers at Rothamsted and at the Pest Infestation Laboratory of the D.S.I.R.

Although the principal peacetime use of pyrethrum is for fly sprays, pyrethrum insecticides, owing to their non-poisonous nature, possess advantages for various horticultural purposes. They have proved especially useful in gardens and glasshouses and for specialized purposes, such as the control of pests attacking mushrooms. Pyrethrum dusts have steadily gained in popularity and being non-poisonous appear to be specially suitable for the control of certain pests on fruit by spraying from aircraft. Various authors have claimed that the pyrethrins possess anthelmintic properties, but other workers have been unable to substantiate the claims.<sup>11</sup> It has been found, however, that ointments containing pyrethrum can be used successfully in the treatment of scabies and for the control of other external parasites.

Potter<sup>24</sup> discovered that the Indian meal moth (*Plodia interpunctella*)



and the cocoa moth (*Ephestia elutella*) were controlled in warehouses by atomizing a solution of pyrethrins in refined heavy petroleum oil. Not only were the adult moths destroyed, but larvae crawling over sprayed surfaces were killed.<sup>25</sup> This toxic film method is used in the "film technique" method of laboratory testing of insecticides.<sup>26</sup> The insecticide used is non-poisonous and non-inflammable, leaving food-stuffs free from taint or injury; and the Potter method of control has, in fact, become a routine practice.

The problems which aircraft travel have introduced into public health have been investigated by Mackie and Crabtree<sup>27</sup> who, in 1938, disinfested aircraft in flight by the use of an aqueous-based pyrethrum insecticide. They used the Larmuth device in which carbon dioxide from a sparklet bulb supplied the pressure to distribute the insecticide throughout the less accessible parts of the aircraft through a system of pipes and for the passenger cabins the Phantomyst nebulizer. The arrangements necessary for successful disinfestation in the air depend upon the ventilation system of the particular aircraft.

The first impact of the pyrethrum mist rouses the mosquitoes, bringing them from their hiding-places into higher concentrations of insecticide.

As recently as 1943, King pointed out<sup>28</sup> that although the hazard of yellow fever has been largely removed by vaccination, it would be a vast undertaking to immunize the entire native population in troop concentration areas. Further, yellow fever is still widespread in Africa and the increase of air travel threatens its spread to India, China and the Malayan region as well as Brazil. The mosquito (*Aedes aegyptii*), carrier of yellow fever, also transmits dengue fever to which troops are not immune. The need for disinfestation is further emphasized by the observation of Ramsey<sup>29</sup> that more than 2,000 aircraft were examined at Khartoum during the period July, 1935, to August, 1938, and, excluding common house-fly varieties, the total number of specimens of insects counted was 1,960, comprising no less than 146 species. Dunna-hoo<sup>30</sup> has reported that, at the experimental disinfestation base established at Trinidad on the principal air route from South America, the spraying of an extract of pyrethrum with a special power-spraying apparatus, thirty minutes before take off, has provided efficient disinfestation but that more recently, the aerosol bomb (considered later)



has been used effectively. The possibility of transporting mosquitoes is not confined to aircraft; in 1943, Eyles<sup>31</sup> noticed that mosquitoes which entered a car at Reelfoot Lake were still alive after travelling 120 miles (five-hour journey) to Memphis which suggested an explanation of cases of malaria contracted in localities supposedly free of *Anopheles*.

The killing of adult mosquitoes with pyrethrum sprays is now recognized as a major anti-malarial measure and Covell<sup>32</sup> regards this method as one of the most important advances made in malaria prevention in recent years.

According to Longworth,<sup>33</sup> pyrethrum larvicides are improved by the addition of materials such as cresylic acid and pine oils. The New Jersey pyrethrum larvicide has been used extensively in the U.S. and it has been found<sup>34</sup> that the toxicity can be increased by the addition of synergists which are of growing importance as adjuvants to the pyrethrum sprays used against flying insects. In seventy-five U.S. patents issued during the period February, 1938, to June, 1941,<sup>35</sup> about 1,400 organic compounds were proposed as substitutes for pyrethrum, including 339 thiocyanates and four *iso*-thiocyanates. Most of these compounds were not described as themselves effective but as being able to replace the pyrethrins partially, thus acting as "activators" or "boosters" or "synergists". The most successful of the commercially available synthetic materials able to replace entirely pyrethrins in fly-sprays are lethane ( $\beta$ -butoxy- $\beta$ -thiocyanodiethyl ether<sup>36</sup>) and thanite (fenchyl thiocynoacetate<sup>37</sup>—see Chapter XIII).

The following are typical of the materials which have been reported as activators or synergists for pyrethrum:  $\alpha$ -naphthyl *iso*-thiocyanate<sup>38</sup> (Kesscocide); ethylene-glycol-ether of pinene (D.H.S. Activator)<sup>39</sup>; acetylated 1 : 3-indandiones<sup>40</sup>;  $\alpha\beta$ -dibromo- $\beta$ -nitro-ethyl-benzene<sup>41</sup>; piperine, the alkaloid found in the fruits of black pepper<sup>42</sup>; methyl-phenyl-nitrosoamine; 2 : 4-diamyl-*cyclo*-hexanol<sup>43</sup>; *isobutyl*-undecyl-enamide (IN 930)<sup>44</sup>; sesame oil.<sup>45</sup> Recently, allyl phenols have been reported to possess insecticidal properties which were enhanced by the inclusion of further nuclear allyl groups.<sup>46</sup> The  $\gamma$ -thiocyano-propyl and  $\beta$ -thiocyanoethyl ethers of phenols are toxic to flies and in particular, the  $\gamma$ -thiocyanopropyl ether of 1, 3, 5-xyleneol was found to be excellent for use in household fly-sprays because of its toxicity, rapid paralysing



effect and lack of objectionable odour. Dioctylamine is another compound reported to be suitable for fly-sprays.<sup>47</sup> Anderson<sup>48</sup> found that the effectiveness of pyrethrum in oil products against sand flies was increased by pine oil or naphthalene.

In view of its availability, the synergistic effect<sup>49</sup> of sesame oil was investigated by Haller and co-workers. They confirmed the observations of Eagleson of a synergistic effect upon the pyrethrins since sesame oil alone was ineffective and discovered that sesamin was the responsible constituent of the oil. The investigation by Haller, LaForge and Sullivan<sup>50</sup> on the synergistic effect of compounds related to sesamin is highly instructive. Their structure is:

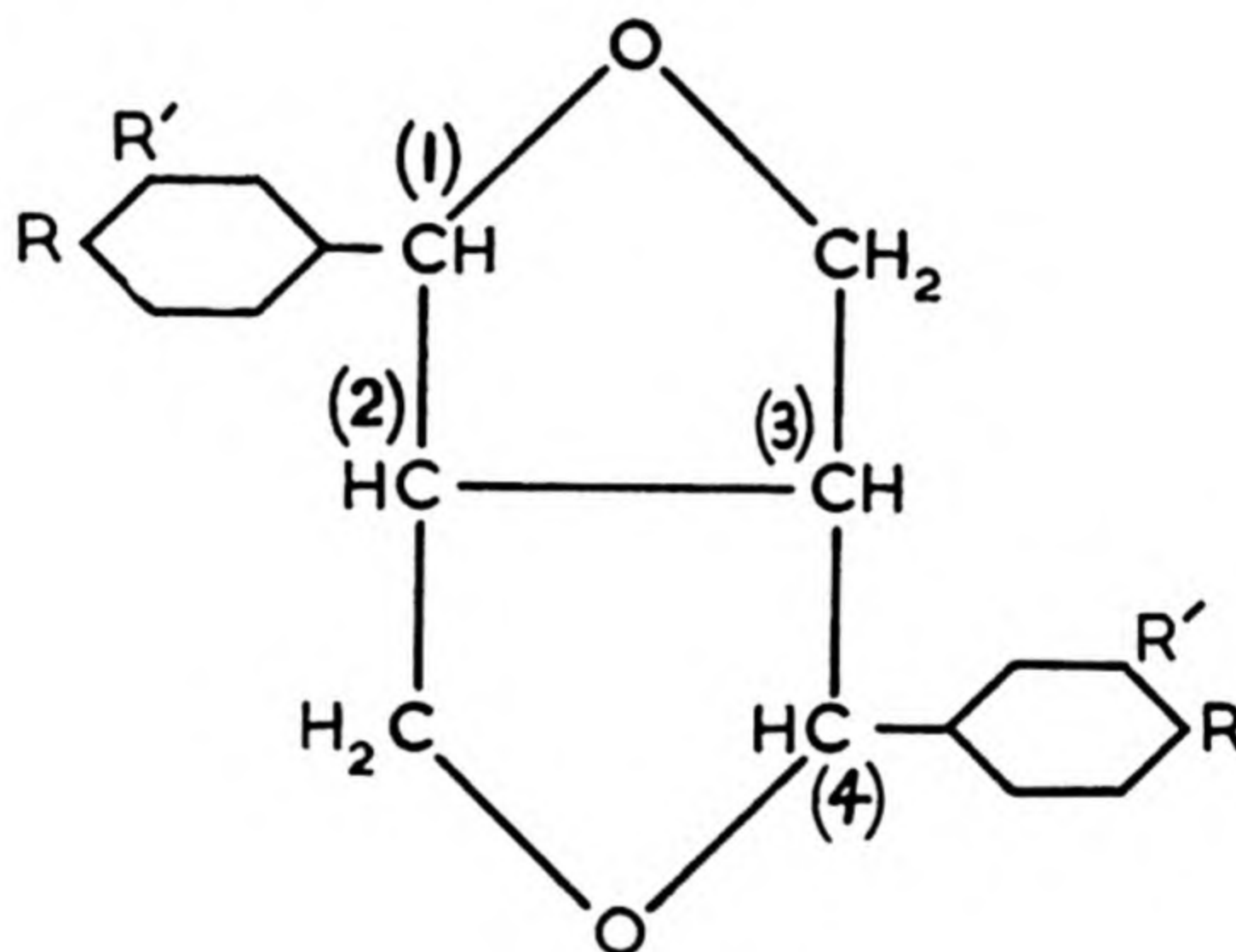


Fig. 31

where  $R, R' = OH$  (methylenedioxy) for sesamin, *isosesamin* and *asarinin*;  $R' = OCH_3$  for *pinoresinol*;  $R = R' = OCH_3$  for *pinoresinol dimethyl ether*;  $R = O_2C.CH_3$ ,  $R' = OCH_3$  for *diacetyl derivative of pinoresinol*. It was found that *isosesamin* and *asarinin* were as effective as sesamin in combination with the pyrethrins in fly-sprays. These compounds have the same structure but differ in the configuration on carbon atoms (1), (2), (3) and (4). *Asarinin* is the optical antipode of *isosesamin* which is obtained by treating sesamin with hydrochloric acid. This independence of spatial configuration on the



synergistic activity is noteworthy; with many insecticides (nicotine, rotenone, deguelin and toxicarol) optical activity has an important bearing on the insecticidal effect.<sup>51</sup> Since pinoresinol and its dimethyl ether and diacetyl derivatives were without appreciable synergistic action it appears that the nature of the substituents on the benzene ring is the only determining factor in the action of this class of compounds. Furthermore, the work opens up a field which may lead to the discovery of other synergists—probably more active—for pyrethrins.

The immense importance of the medium or carrier in which the insecticide is dissolved has been fully recognized<sup>52</sup> only recently. Hurst has shown that the activity of the pyrethrins is more pronounced in a light than a heavy mineral oil due to the enhanced penetration of the toxicant induced by the lighter oils. This factor is undoubtedly of importance in devising methods of bioassay and after criticism of the Peet-Grady method, test systems were proposed which will provide an index, not only of kill, but also of the nature of the intermediary chain of biological responses which appears to be of special importance in synergistic action.

During the past three years, interest has been revived in incense-type smokes produced by burning pyrethrum and derris, a subject reviewed by Brightwell.<sup>53</sup> The Japanese exports of such manufacture—probably largely pyrethrum products—rose from 790 tons in 1930 to 1,850 in 1939. The toxic effect of pyrethrum smoke is due to the products of combustion which consist of a complex mixture of aldehydes, acids, phenols and other bodies, and it would appear, therefore, that this use of pyrethrum is wasteful and ineffective. American chemists developed a method of preparing aerosols which involved the spraying of a solution of pyrethrum extract in alcohol or safrole<sup>54</sup> on to a hot plate at 375° C. The dense cloud produced was effective against flies and mosquitoes and produced a high mortality when used against bed bugs.<sup>55</sup> The use of surface-active agents increased the effectiveness of most aerosols and it was pointed out that as these compounds reduced the energy required for disintegration the resulting reduction in particle size was probably a factor. Roark<sup>56</sup> pointed out that the word aerosol was first suggested by Donnan in 1923, to denote a system of particles of ultra-microscopic size dispersed in a gas. It is unfortunate that the



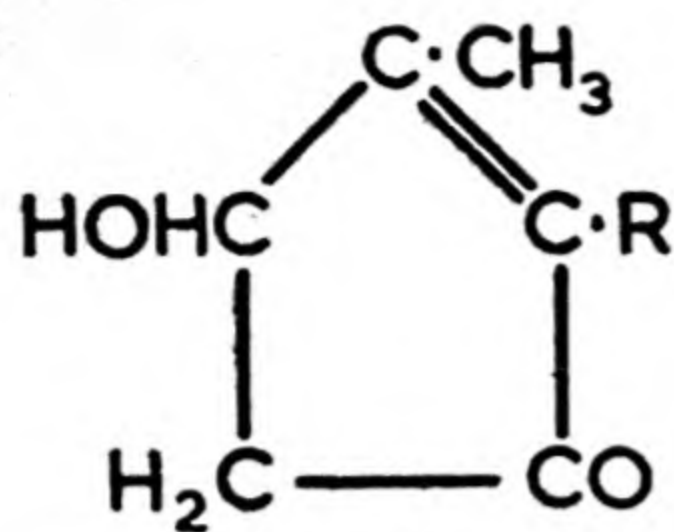
word has been used in America as a trade mark for wetting agents for use in reducing the interfacial tension between two liquid phases or a solid and liquid phase. In the so-called aerosol bomb<sup>57,58</sup> pyrethrum extract, D.D.T., and sesame oil are dissolved in dichlorodifluoromethane (Freon) which at room temperature has a pressure of about 90 lb. per square inch so that the use of a hot plate is unnecessary. When this solution was released through a suitable atomizing nozzle, the aerosol produced was very toxic to mosquitoes and other insects and the particles produced were so minute that the settling rate was low. It seems<sup>59</sup> that more than twelve years ago self-propelling containers were demonstrated in America using carbon dioxide with petroleum ether as solvent for the pyrethrum extract. The high pressure container required made the cost prohibitive at that time, although the dilution of the carbon dioxide with acetone or alcohol in order to reduce its high vapour pressure of 1,000 lb. per square inch was suggested. The advantages of the aerosol bomb are its durability, instant readiness for use and non-requirement of spray equipment. During the war, the British Services put into use an individual sprayer known as the "Bulb Sparklet Individual Insecticide Sprayer".<sup>58</sup> This apparatus consisted of a "Sparklet" bulb with a dip tube connected to a tip which on breaking, permitted the contents to discharge. The insecticide used consisted of a solution of D.D.T., pyrethrum extract and sesame oil in a mixture of acetone, chlorobenzene and kerosene; the propellant was carbon dioxide.

In spite of recent great advances in the preparation of synthetic insecticides, pyrethrum flowers, on account of their superb "knock-down" action and non-poisonous nature, remain one of the most important insecticides and are being grown extensively.

As a result of further work<sup>60,61</sup> since this account was prepared, it has now been suggested that structure (A) should be assigned to the ketonic constituents of the pyrethrin and cinerin molecules rather than the structure (B) formerly regarded as correct.

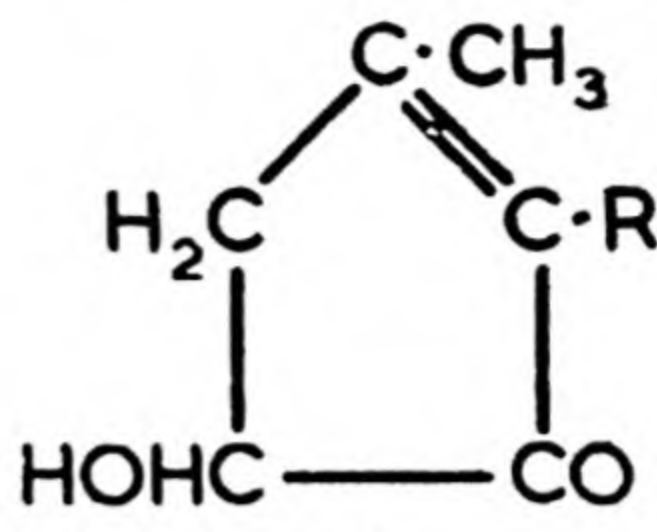
LaForge and Barthel<sup>62</sup> prepared the pyrethrins and cinerins by partial synthesis and reported that, in biological tests against houseflies, Pyrethrin I was 1.5 times as toxic as Cinerin I; Pyrethrin II was 1.3 times as toxic as Cinerin II; Pyrethrin I was 4.0 times as toxic as Pyrethrin II; Cinerin I was 4.0 times as toxic as Cinerin II. The toxicity





A

Fig. 32



B

Fig. 33

R = C<sub>4</sub>H<sub>7</sub> for cinerolone

R = C<sub>5</sub>H<sub>7</sub> for pyrethrolone

in all cases was independent of the presence of optical activity in the alcoholic ketone component, *i.e.* whether the compound had been prepared from dextro or racemic pyrethrolone or cinerolone.

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## CHAPTER XIII

### LETHANE AND THANITE

THE plants from which pyrethrum and rotenone insecticides are obtained are not indigenous to the United States. Consequently, efforts have been made to produce a synthetic chemical which would replace, wholly or in part, these natural materials. From these efforts, the synthetic insecticides lethane and thanite have been developed.

#### Lethane

The lethanes are organic thiocyanates which act as contact poisons and have found wide use for the control of household and agricultural pests. Unlike pyrethrum, the lethanes are stable to light and consequently do not lose their toxicity on storage.

Lethane 384 is a 50 per cent. solution (by volume) of  $\beta$  butoxy  $\beta$  thiocyano diethyl-ether ( $C_4H_9O(C_2H_5)_2O(CH_2)_2CNS$ ) in a petroleum distillate base.<sup>1</sup> It is a clear pale liquid with a specific gravity of 0.910 to 0.933 at 20° C.

Lethane 60 is a 50 per cent. solution of  $\beta$ -thiocyanethyl-laurate ( $C_{11}H_{23}COO(CH_2)_2CNS$ ) in a petroleum distillate base.<sup>1</sup>

Lethane 384S is a 1 : 3 mixture of lethane 384 and lethane 60.<sup>1</sup> It is a clear pale liquid with a specific gravity of 0.920 at 20°C.

Murphy and Vandenburg<sup>2</sup> reported that a 4 per cent. solution of lethane 384 gave a 100 per cent. knockdown of houseflies in three minutes and a 78 per cent. mortality after twenty-four hours. In tests using lethane 384 alone and mixed with pyrethrum or rotenone, it was concluded that the substitution of small percentages of lethane 384 for part of the pyrethrum or rotenone increased both the knockdown and kill.

Recently, Busvine<sup>1</sup> compared the toxicity of a number of insecticides, including lethane 384, 384S and 60, to the louse and the bedbug; the results are summarized in Table 8.

Walker and Anderson<sup>3</sup> compared the toxicity of rotenone and



rotenone-lethane 60 dusts for the control of the pea aphid and found that dusts containing rotenone in addition to lethane 60 gave significantly better results than did similar dusts without lethane 60.

TABLE 8

Insecticide	Median lethal concentration	
	Body lice per cent.	Bedbugs per cent.
Gammexane .. .. .	0.016	0.051
Pyrethrins (in the presence of 2 per cent. <i>iso</i> -butyl undecyleneamide) .. .. .	0.038	0.026
D.D.T. .. .. .	0.30	0.56
Pyrethrins .. .. .	0.47	0.045
Lethane 384 (active principle) .. .. .	1.5	4.0
Lethane 384 Special (active principle) .. .. .	2.4	12.5
Thanite .. .. .	3.2	75
Lauryl thiocyanate .. .. .	6.0	19.5
<i>bis</i> Ethyl xanthogen .. .. .	6.2	75
Lethane 60 (active principle) .. .. .	8.1	32
Benzyl benzoate .. .. .	21	75

Schwitzgebel<sup>4</sup> has reported that a mixture of lethane A-70 (90 per cent.  $\beta$   $\beta'$ -dithiocyano diethyl ether) and D.D.T. gave a better kill of American and German cockroach than D.D.T. alone. A dust containing 5 per cent. lethane A-70 and 5 per cent. D.D.T. was found superior to either toxicant used alone at a strength of 10 per cent. A dust containing 5 per cent. lethane A-70 with 10 per cent. of D.D.T. paralysed 94 per cent. of German cockroaches in one hour as against none for D.D.T. alone at 10 per cent.

Lethane B-71 is a dust containing 15 per cent. of lethane A-70 (thereby giving 13.4 per cent. of  $\beta$   $\beta'$ -dithiocyano diethyl ether) 5 per cent. of magnesium carbonate and 80 per cent. of talc. This insecticide is used for the control of aphids, leafhoppers and similar soft-bodied insects.

Murphy<sup>5</sup> has reported the results of tests carried out to determine the toxicity of lethane 384 to a number of different animals. The results are summarized in Table 9.



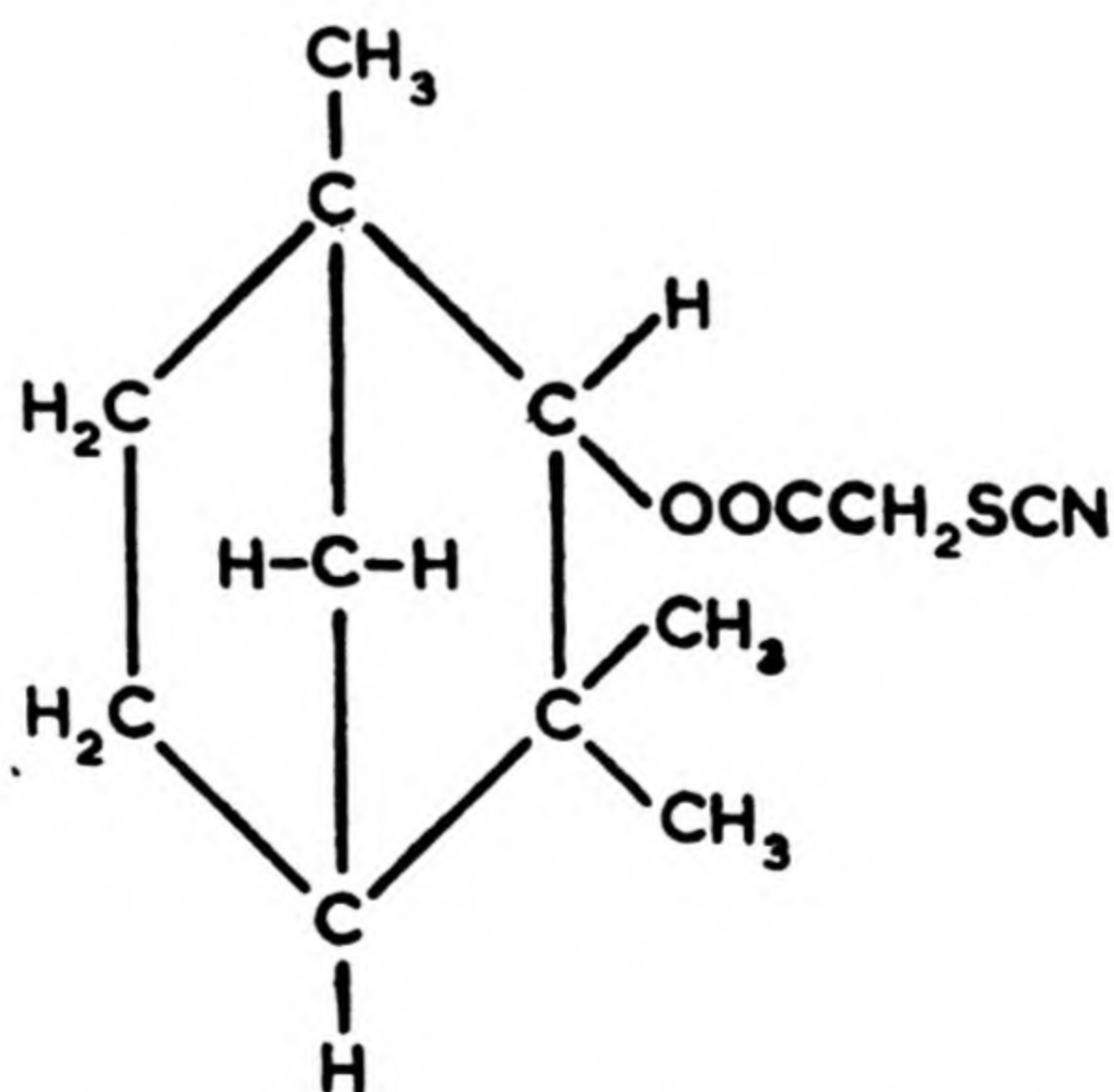
TABLE 9

M.L.D. for Lethane 384 as determined by Wallace Expressed as ccs. per kilogram Administration						
Animal	Intra-peritoneal	Mouth	Sub-cutaneous	External	Stomach	
Rat .. ..	0.06	0.8	0.6	0.7	—	
Cat .. ..	0.06	0.2	0.2	—	0.075	
Dog .. ..	0.06	—	0.4	—	—	
Rabbit .. ..	0.06	0.15	0.125	0.3	0.1	
Guinea Pig ..	0.06	0.3	0.45	5.0	—	

From these figures it was considered that lethane 384 displayed no significant health hazard.

### Thanite

Pierpont<sup>6</sup> reported that of a number of products tested fenchyl thiocynoacetate

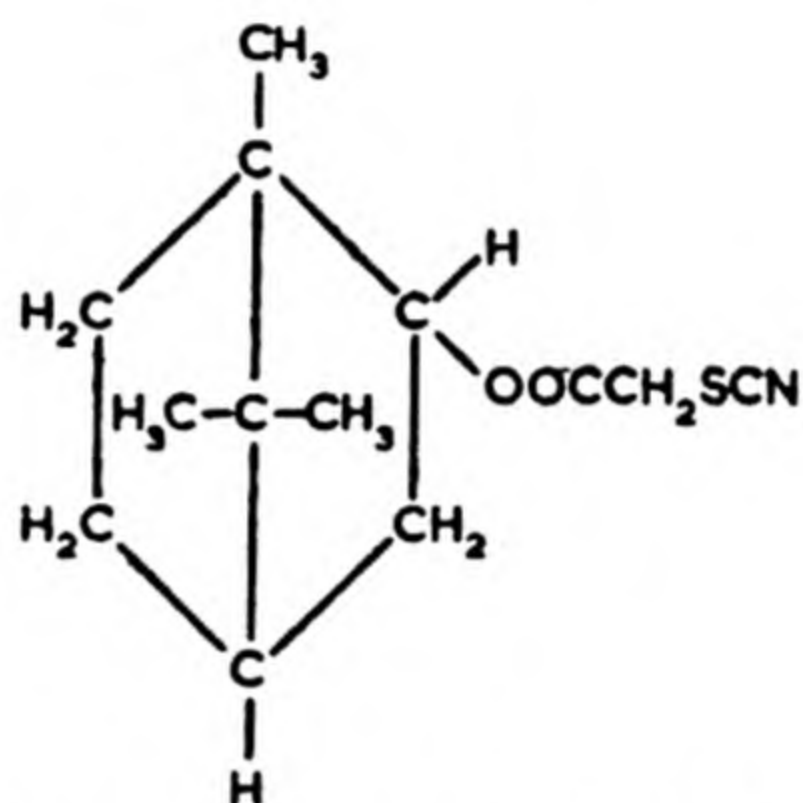


FENCHYL THIOCYANOACETATE

Fig. 34



showed outstanding insecticidal properties. This was prepared by reacting alkyl halogen esters of secondary alcohols (derived from secondary alcohols fractionated from pine oil) with sodium thiocyanate. However, the quantity of fenchyl thiocynoacetate which could be prepared would not have been sufficient to meet the needs of the insecticide industry. During the preparation of the fenchyl ester it was noticed that bornyl and *isobornyl* thiocynoacetate, both having similar physical and chemical properties to the fenchyl ester, were produced.



BORNYL AND ISOBORNYL THIOCYANOACETATE

Fig. 35

Further investigation<sup>6</sup> showed that *isobornyl* thiocynoacetate could be prepared from camphene. The materials from which camphene can be prepared (by isomerizing  $\alpha$ - or  $\beta$ -pinene, or the conversion of pinene to bornyl chloride and then the removal of hydrogen chloride) are in plentiful supply, the pine forests supplying large quantities of raw materials. Later<sup>6</sup> it was shown that the thiocyno esters could be prepared from pinene or turpentine, the finished product being very similar to that obtained from the secondary alcohols obtained from pine oil.

It was concluded<sup>6</sup> that the thiocynoacetates of fenchyl, bornyl and *isobornyl* alcohols possessed similar chemical, physical and insecticidal properties. This mixture, which contained approximately 82 per cent. of *isobornyl* thiocynoacetate, has been given the trade name "Thanite".

Thanite is a brownish viscous liquid having a camphor-like odour, is



insoluble in water but soluble in all proportions of base oils. When diluted, it is almost colourless and is slightly irritating when atomized under pressure. Applied in deodorized kerosene and in the normal manner thanite had no deleterious effect upon plastered walls, wall-paper and linoleum.<sup>6</sup>

Pierpont reported that thanite is chemically stable under normal storage conditions. When stored in flint-glass bottles for five months and exposed to diffused and direct sunlight, or stored in lead-lined containers for twelve months, there was no loss in toxicity. Aluminium tin-lined containers, glass, cork, hard rubber, white oak barrels and zinc were apparently unaffected by thanite but galvanized iron was slowly corroded.<sup>6</sup>

Pyrethrum, rotenone and lethane 384 Special are compatible with thanite.

Thanite, which is a contact poison, has found wide application in the formulation of insecticides for household and veterinary use.

Studies of acute and subacute toxicity tests with laboratory animals showed that extreme exposures to Thanite produced primary irritation but no progressive local damage; recovery from ill effects was rapid upon removal from exposure.<sup>6</sup>

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CHAPTER XIV

CHLORINATED PERSISTENT INSECTICIDES

D.D.T.

Introduction

GREAT discoveries are sometimes the result of a chance observation or a flash of genius but—especially in these days of intensive and extensive research—more frequently the result of a long and well-planned sustained effort. The discovery of the insecticidal properties of D.D.T. is a good example of this planned method which can lead occasionally to dazzling practical results.

For many years the attention of the research laboratories of The Geigy Company in Switzerland had been directed to the preparation of moth-proofing materials. As a result of this work, the Swiss scientists concluded that one of the requirements for a good stomach poison against clothes moth larvae was the presence of a p, p'-dichloro-diphenyl grouping in the molecule. The product finally marketed under the name "Mitin FF" possessed the following structure<sup>1</sup>:

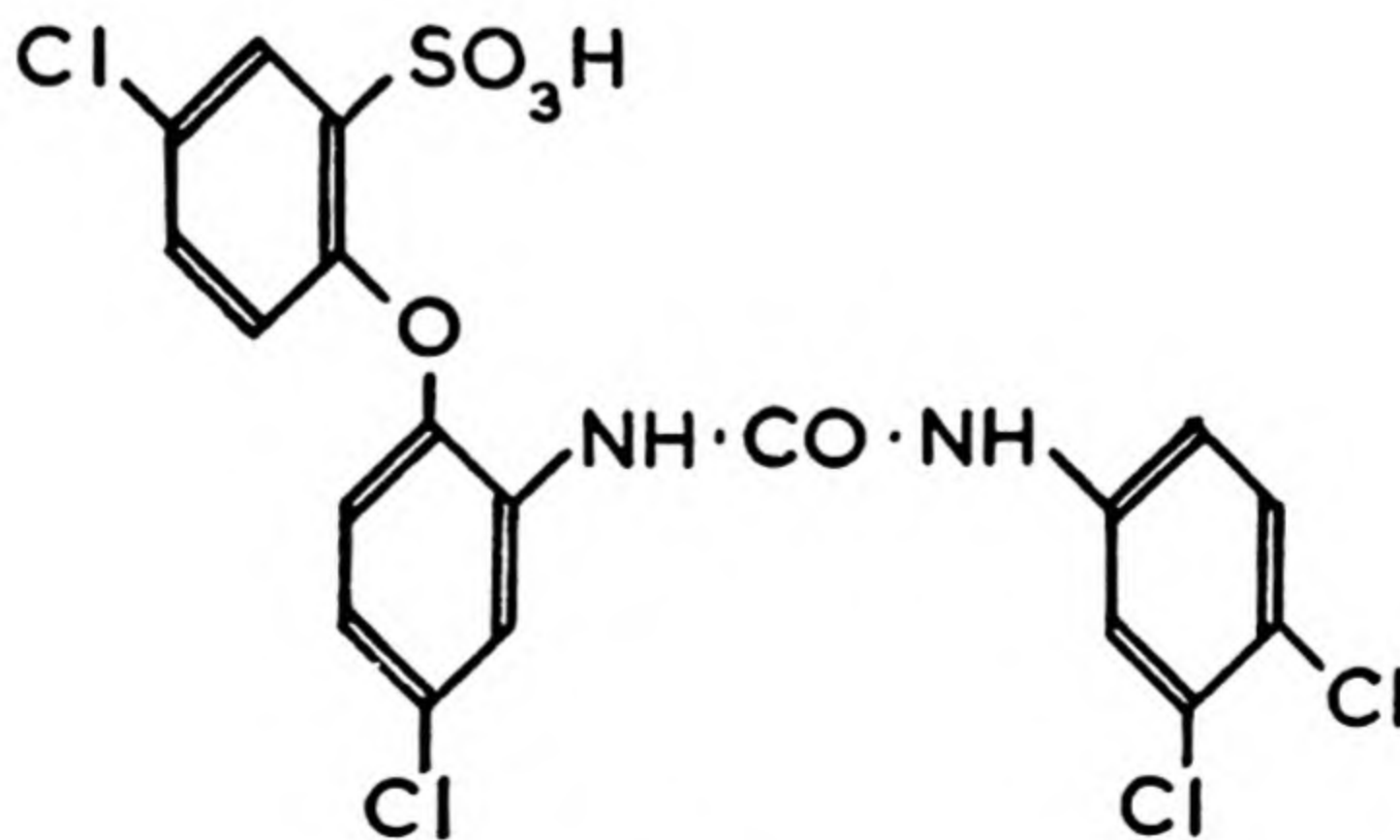
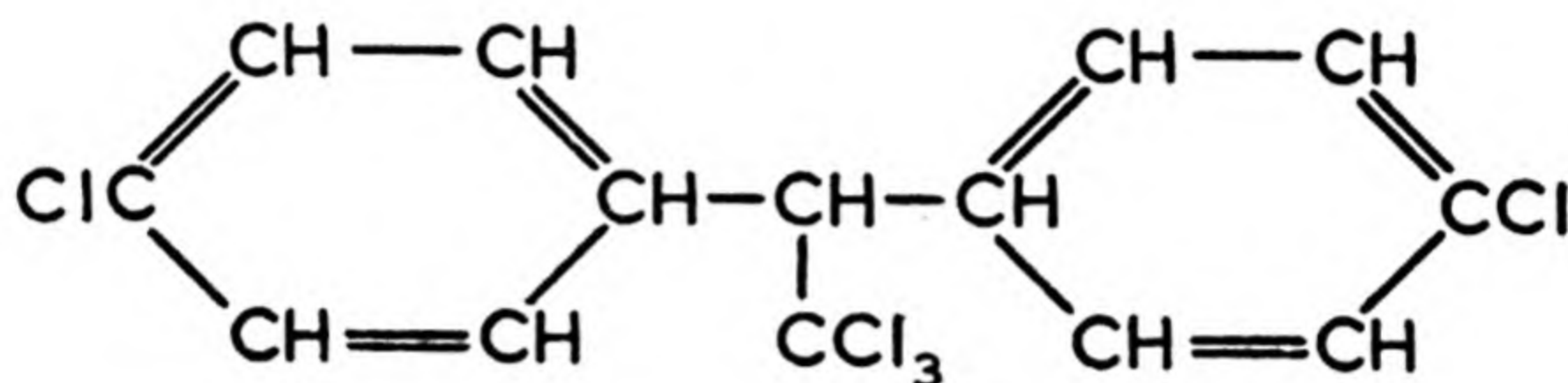


Fig. 36



It was at this time that the work was extended to investigate as contact insecticides the numerous synthetic chemicals being produced in connection with the moth-proofing experiments. After following these lines of research for some years, the Swiss workers<sup>2</sup> finally discovered the remarkable insecticidal properties of the compound now known throughout the world as D.D.T. (Although this compound had been prepared in 1874 by a student named Othmar Zeidler<sup>3</sup> the insecticidal properties had been unsuspected).



D. D. T.

Fig. 37

Several theories have been advanced<sup>2,4,5</sup> to explain the reason for the extraordinary efficiency of this compound but further consideration of the mode of action is outside the scope of this book.

It is essential to mention, however, that not only is D.D.T. a most potent contact insecticide but it is also an excellent stomach poison. Thus as a contact insecticide, the Swiss workers<sup>6</sup> computed that  $10^{-5}$ g of D.D.T. per square cm. of a glass surface would kill flies, *i.e.* 1 oz. spread uniformly over 3,000 million square feet of glass would provide under ideal conditions a surface capable of killing flies brought into contact with the surface. As a stomach poison, Martin and co-workers<sup>6</sup> found that a dose of the order of 0.01 mg. was sufficient to kill a cabbage moth caterpillar, *i.e.* 1 oz. kills, under ideal conditions, 3,000,000 of the caterpillars.

D.D.T. itself is a white powder and the commercial product available in this country contains about 80 per cent. of the toxic "para-para isomer". Pure "para-para" D.D.T. melts at 107–108° C. but the commercial product melts somewhat indefinitely and sinters at about



90° C. (According to K. H. Cook and F. A. Cook<sup>7</sup> when the para-para/compound is purified by special methods a melting point of 110–110.5° C. is attainable.) It is remarkably stable and is practically non-volatile and has the amazing property of providing surfaces which remain toxic to insects for very long periods after the D.D.T. has been applied.

The applications of D.D.T. are extremely wide—this is due not only to the dramatic residual effect but also to the extraordinary range of insecticidal activity. Thus it kills insects of the most simple and primitive types as well as some of the most highly developed and complex. This can be illustrated by the fact that D.D.T. is effective against the cricket (one of the most primitive insects) and the fly (one of the most complex and highly developed members of the insect world).

Disease has been from Biblical times one of the main factors in deciding the outcome of campaigns and the fate of armies. On the other hand, it is within living memory that the true importance of insects as vectors of diseases such as typhus (carried by the louse) and malaria (transmitted by the mosquito) has been recognized. During the second world war, the struggle to gain at least regional mastery of those insects inimical to man was intensified and considerable progress made due largely to the development of D.D.T. In this chapter, we have included references to other compounds of this class of “chlorinated persistent insecticides”—some of which appear to have emerged, not unnaturally, as a result of the intensive work which has been devoted to the preparation and examination of chlorinated hydrocarbons since the full implication of the discovery of the insecticidal properties of D.D.T. has been realized.

### Manufacture and Chemistry

D.D.T. is prepared by condensing chlorobenzene with chloral in the presence of suitable condensing agents<sup>8</sup> such as sulphuric acid. To-day, the proportion of p, p'-isomer (I) in the commercial product is usually about 80 per cent. and the product contains as main impurities a proportion of the o, p'-D.D.T. isomer (II) together with a proportion of the half-condensation product (III)



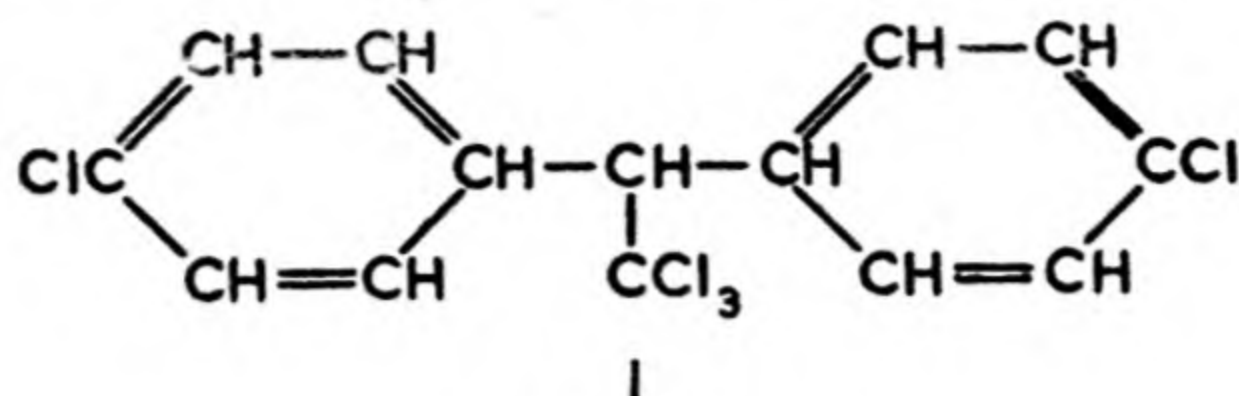


Fig. 38

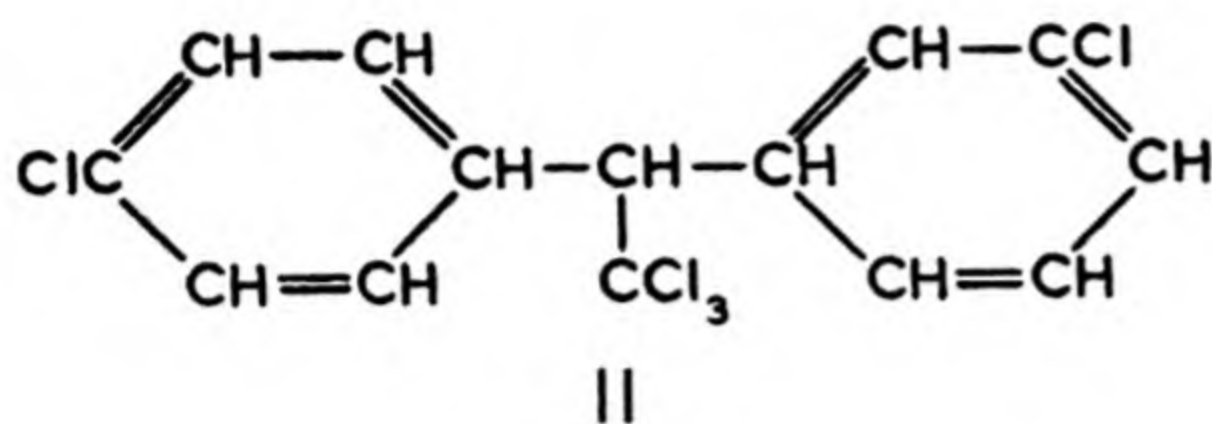


Fig. 39

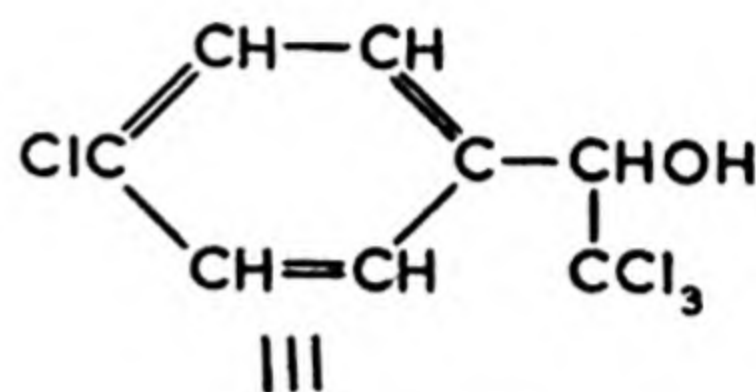


Fig. 40

There are a number of impurities which are present in small proportion and Haller and co-workers<sup>9</sup> confirmed the presence of at least fourteen different compounds. Recently Cristol, Haller and Lindquist<sup>10</sup> have isolated, with considerable difficulty, from technical D.D.T. a proportion of the ortho-ortho' isomer (IV)

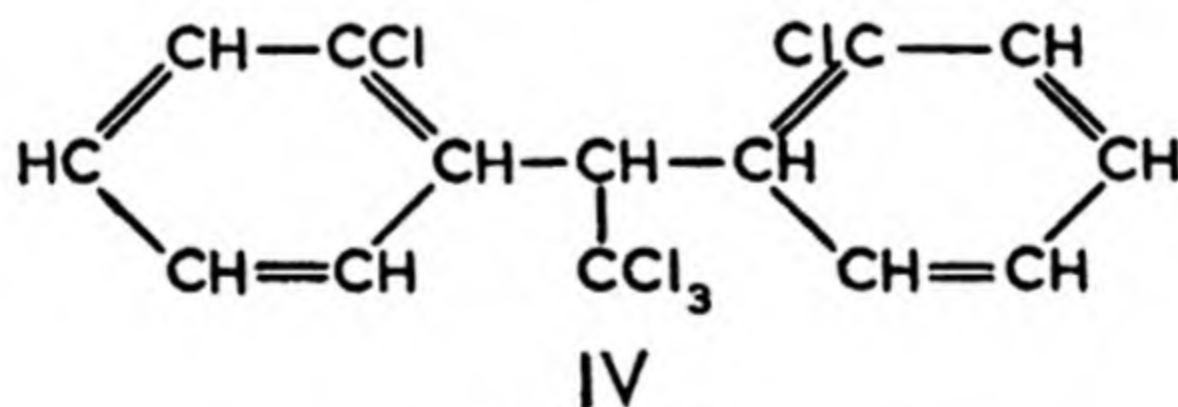


Fig. 41

In tests against houseflies under strictly comparable conditions, the para-para'-isomer was shown to be of much higher toxicity than either the ortho-para or ortho-ortho' isomers. For instance, it was found that o, o'-D.D.T. and o, p'-D.D.T. gave no kill at a concentration of 0.2 per cent. in kerosene whereas p, p'-D.D.T. produced 100 per cent. kill at this concentration. Technical D.D.T. is a slightly waxy material and it is necessary to grind the D.D.T. first with roughly its own weight of diluent (such as talc) before further dilution to the customary percentages of 2 to 10 per cent. of active ingredient according to the purposes



for which the dust is desired.<sup>6</sup> The insecticide is also used in the form of wettable (or spray) powders, for mixing with water before application as a suspension, solutions in organic solvents, emulsions, as an aerosol, and as a constituent of certain paints. It has recently been found that effective D.D.T. insecticidal smokes can be produced by suitable combustion methods.<sup>11</sup>

### **Toxicity to warm-blooded animals**

In the present work it is clearly impossible to enter into detailed consideration of the effect of D.D.T. upon warm-blooded animals which has been reviewed elsewhere.<sup>6</sup> Neal and von Oettingen<sup>12</sup> have recently summarized the results to date and the following conclusions are drawn. D.D.T. is definitely less toxic to warm-blooded animals than Paris green or sodium fluoride and is not harmful to man if properly used. When D.D.T. is ingested by accident it should be removed from the stomach or intestine as rapidly as possible. In dust form the compound is not absorbed through the skin but in oil solutions it is readily absorbed. Thus oily solutions should not be allowed to remain on the skin for any length of time and precautions should be taken not to saturate clothing. When the skin has been exposed to covering with oily solutions or concentrates, the area should be washed and wet clothing changed. In general, it is not desirable to apply D.D.T. solutions to the coat or skin of animals and food should be removed during distribution of D.D.T. insecticides to avoid the possibility of contamination.

### **Toxicity to arthropods**

As already mentioned, D.D.T. appears to be toxic to the majority of arthropods but the true Insecta seem to be more susceptible than other classes; thus the compounds appear to be of doubtful value against Arachnida. D.D.T. does not exert ovicidal properties and in general does not affect pupae but adults frequently acquire a lethal dose of D.D.T. during emergence because of the persistent residual action. As is to be expected, there is a wide degree of variation in the susceptibility of different species of insects—for instance, Busvine<sup>13</sup> found that the



lethal dose of D.D.T. for *Rhodnius* was much above 10 mg. per sq. cm. of surface; for *Cimex*, about 10 mg.; for adult *Musca domestica*, 1.0 mg.; and *Aedes aegypti*, 0.001 mg. Also, as with other insecticides, the susceptibility of the insect depends not only upon its state of development but upon the sex and environmental factors which can determine such factors as the physical activity of the particular insect. In general practice, of course, the concentrations of the insecticide employed far exceed applications of the order mentioned above.

### D.D.T. against pests affecting man and animals

**Flies.**—During recent years, the role of the housefly (*Musca domestica*) in spreading disease has become increasingly recognized—the disease organism can be carried externally on the body of the fly, in the excrement which is voided as it passes over food and other surfaces, or in the vomit which is sometimes deposited in order to render food suitable for sucking up by the mouth parts (proboscis). Fortunately, these insects are very susceptible to D.D.T. and the effects upon flies have been studied carefully.<sup>2</sup> When these insects come into contact with D.D.T., a short period of excitement takes place followed by a slow progressive paralysis which first affects the legs. It becomes difficult for the flies to walk correctly although flight is possible; at a later stage paralysis spreads and becomes more acute so that the insects make crawling movements but little progress and turn over on to their backs making convulsive movements and finally die. Whereas with some insecticides recovery is possible, it has been observed that flies did not escape death after exhibiting the first symptoms of paralysis. However, D.D.T. does not “knockdown” insects rapidly and to obtain quick results, it is essential to add to the D.D.T. solution one of the older insecticides such as pyrethrum extract. A number of reviews of the literature on the use of D.D.T. in controlling flies are available<sup>14,15,6</sup> The advent of D.D.T. with its dramatic residual effect has somewhat complicated the methods of control for various insects and the development in the control of flies, mosquitoes and bedbugs illustrate the influence which the insecticide has exerted. These remarks apply equally to the other chlorinated persistent insecticides of this group which are



dealt with later. In pre-D.D.T. days it was customary to control flying insects, such as flies and mosquitoes, by discharging into the air sprays made up with toxicants such as pyrethrum which paralysed rapidly and killed a proportion of the insects. When D.D.T. is applied to a surface, a long-term residual toxic action is obtainable and in the Services during the war extensive use was made of a 5 per cent. solution of D.D.T. in kerosene for this purpose.

The standard British Army fly and anti-mosquito spray (space spray) against flies and mosquitoes for general purposes during the war had the specification:

- 0.07 per cent. pyrethrins
- or 0.05 per cent. pyrethrins plus 0.3 per cent. D.D.T.
- or 0.03 per cent. pyrethrins plus 0.5 per cent. D.D.T.

An alternative method of destroying flying insects is by the use of the so-called aerosol bomb.<sup>16</sup> This consists of a metal container charged with pyrethrum extract, D.D.T. and sesame oil in a solution of dichlorodifluoromethane (Freon) which at room temperature has a pressure of about 90 lb. to the square inch. When the solution is released through a suitable orifice the aerosol produced is very toxic to mosquitoes and other insects and the settling rate is low so that the fine fog of particles suspended in the air persists for considerable periods. Such a method is very useful in ensuring that aeroplanes are free of insects—especially in these days of rapid aeroplane transportation—to prevent carrying disease vectors from one country to another. The aerosol bomb which is an American invention is manufactured in various sizes but the most popular holds about one pint of the solution and has the appearance of a small vacuum flask. While the container has liquid in it, the fog can be produced and turned off at will. On the other hand, the British Individual Sprayer (in which the propellant is carbon dioxide<sup>14</sup>) discharges its contents in six to eight seconds disinfesting 500 to 1,000 cubic feet and cannot be turned off. (These individual sprayers were issued to men of S.E.A.C.) Reference has already been made to the very striking residual effect with D.D.T. For instance, Lindquist and co-workers<sup>17</sup> sprayed one wooden box with a 5 per cent.



solution of D.D.T. in kerosene and another box with a 5 per cent. solution of D.D.T. in a mixture of *cyclohexanone* and deodorized kerosene at the rate of 125 mg. of D.D.T. per square foot and obtained kills of 65 and 86 per cent. respectively by exposing flies in the sprayed boxes for only one minute, 158 days after these had been treated with the sprays. It has been found<sup>6</sup> that the incorporation of as little as 0.5 per cent. D.D.T. in oil-bound water paint will provide a surface toxic to flies for more than a year. It has been claimed<sup>18</sup> that as the D.D.T. in this form is less available for contact with the insect than a freshly applied deposit of a D.D.T. solvent spray, the latter is preferable in controlling rather more resistant insects such as the bedbug. It has been pointed out that further work on the period for which surfaces treated with D.D.T. remain effective is necessary before the two methods can be compared. In connection with the residual effect of D.D.T., attention must be directed to the observations of Parkin and Green.<sup>19</sup> These workers sprayed wall boards with solutions containing varying percentages of D.D.T. and after storage for four days under standard conditions of temperature and humidity, houseflies were confined on the treated surfaces beneath Petri dishes. It was found that the best results were obtained when the solutions were more highly concentrated (based on a given amount of D.D.T.) and that when these same samples of wall board were tested after four weeks the surfaces had increased in their toxicity to flies. When the surfaces sprayed with these more highly concentrated solutions were examined microscopically, the D.D.T. was found to be deposited in the form of minute crystals. In this connection, Campbell and West<sup>20</sup> found that a film of coumarone resin containing D.D.T. (equal parts) was very effective against flies and this was considered due to the fact that the D.D.T. formed microcrystals at the surface of the resin film. These points have been mentioned at this stage to draw attention to the numerous factors involved in assessing the optimum conditions for exploiting the residual effect of D.D.T. under various circumstances. Thus the type of surface, whether porous or otherwise, the type of formulation (emulsion, solvent, wettable powder) and climatic conditions all influence the results achieved. For instance, it has been observed<sup>21</sup> that in the spraying of native mud huts under certain conditions with the customary 5 per cent.



solution of D.D.T. in kerosene, a considerable proportion of the solution applied appeared to be absorbed and it may well be that the use of wettable powders may give a more satisfactory long-term effect under these conditions.

Simmons and Wright<sup>22</sup> sprayed cow manure heaps with a diluted emulsion containing 0.1 per cent. of D.D.T. at the rate of 0.6 (U.S.) gallons per cubic foot and during sixty-seven days observed only thirteen flies to emerge from the two heaps treated with the insecticide, whereas 555 flies emerged from control heaps. Other workers<sup>23</sup> in the U.S. reported that D.D.T. insecticides were as satisfactory as phenothiazine and more so than thiourea and borax in preventing houseflies breeding in poultry manure. On the other hand, Crauford-Benson,<sup>24</sup> working in Italy, reported that larvae appeared to avoid the action, if any, of insecticides such as D.D.T. or benzene hexachloride by migration into the manure or refuse and away from the treated surface. The treatment of manure and refuse heaps with persistent insecticides was considered advantageous because adult flies were killed on emergence by contact with the insecticidal surfaces.

**Mosquitoes.**—Malaria, a disease which is transmitted by a wide variety of anopheline mosquitoes, is one of the greatest scourges of the world. It was stated<sup>25</sup> recently that “no disease exceeds it in its toll of death and suffering; it affects up to 300 millions of the world’s population each year with an annual death-roll certainly not less than three million and probably much higher”. The control of mosquitoes is one of the major factors in preventing malaria and the success of D.D.T. against these insects has been spectacular. This insecticide is effective against both adults and larvae. For instance, the application of a 5 per cent. solution of D.D.T. in oil to the surface of mosquito-breeding areas at the rate of only one to two quarts per acre, not only killed larvae but caused breeding to cease for several days.<sup>25</sup> Hand or power spraying equipment can be employed to treat small areas, but in cases where access from the ground is difficult, spraying from aircraft has been used with great success and large areas have been treated by this method of application. Very efficient equipment for use with aircraft has been described<sup>26</sup> and a considerable amount of work has been carried out in the United States to determine the minimum concentration of D.D.T.



required in the field to control mosquitoes so that the danger to fish and wild life is reduced to a minimum.<sup>27</sup> The most efficient spray for controlling adult mosquitoes in dwellings, etc., consists of a kerosene solution containing a mixture of D.D.T. and pyrethrum (or similar rapid knockdown agents such as an organic thiocyanate), the latter producing rapid knockdown and the former ensuring a high kill of the insects. Although D.D.T. is extremely lethal to insects, it lacks the spectacular knockdown and rapidity of action which is characteristic of pyrethrum and the organic thiocyanates. These sprays are usually dispersed by means of Flit gun or other hand sprayer which gives a fine mist. Reference has already been made to the so-called aerosol bomb and the individual sparklet disperser which discharges a fog in which D.D.T. and pyrethrum are usually the active ingredients. Another disease, yellow fever, is carried by the mosquito (*Aedes aegypti*) and this pest is also controllable by the general methods outlined above. Although the hazard of yellow fever has been greatly reduced by vaccination, it would be a vast undertaking to immunize entire native populations. Furthermore, yellow fever is still widespread in Africa and the increase in air travel threatens its spread to India, China and the Malayan region as well as Brazil. Quite apart from this, mosquitoes can carry dengue fever for which immunization is so far not possible. It is obviously necessary to attack the mosquito in all stages of development and it is fortunate that D.D.T. is so very effective against both the adult and larval stages. In applying residual films of D.D.T. against mosquitoes, dosages of 50 to 100 mg. per square foot have been recommended.<sup>28,14,29</sup>

**Body lice.**—Prior to 1939, there seems to have been no effective method, sufficiently simple for wide-scale application, of controlling outbreaks of typhus by killing the insect vector responsible—the louse (*Pediculus humanus corporis*). In general practice, if an isolated individual became infested with body lice then the hair was shaved from the body before applying an ointment containing xylene or cresol. This method was, of course, not applicable to large groups of people, especially under the conditions of overcrowding and so on likely to cause a typhus epidemic. A powder containing naphthalene, creosote and iodoform, known as N.C.I. powder, was applied to clothes in an



effort to control the parasites. Under suitable conditions, clothes were exposed in cold climates to the action of extreme cold overnight to kill the louse and the egg or a similar result achieved by exposing the garments to strong sunlight. During the first world war, a candle was often run along the seams of infested clothing and measures such as crushing the lice between the nails were employed. At that time in disinfesting numbers of men special arrangements were made in which the clothes were subjected to heat treatment—a temperature of 140° F. for about ten minutes being sufficient to destroy both adult lice and the eggs. Other treatments involved fumigation with hydrogen cyanide. Naturally the subject of lousicides received careful consideration during the second world war. The method of heat treatment was improved by the development of excellent equipment and the use of hydrogen cyanide was replaced by less dangerous fumigants such as methyl bromide, methyl allyl chloride, trichloroacetonitrile and methyl formate.<sup>30</sup> To replace the N.C.I. powder the British antilouse powder A.L.63 was developed which contained naphthalene and derris with a small proportion of tar acid and was stated to provide protection for five to eight days by one application.<sup>31</sup> In America, the MYL powder, containing pyrethrum, *isobutylundecylenamide* and dinitro anisole was developed whilst in Russia a powder containing diphenylamine was used. Another dust used with success in Russia was given the name “SK” of which the active principle was chlorinated turpentine.<sup>32</sup> It was found that the spraying of garments with solutions of insecticides of the class of organic thiocyanates (trade names “Lethane” and “Thanite”) killed lice and prevented reinfestation for some weeks and special belts were woven to attract lice and impregnated with such materials but these garments caused some irritation to the wearer. It has been thought desirable to indicate some of the methods employed prior to the advent of D.D.T. so that some realization of the impact of this new insecticide can be assessed. In experiments with D.D.T., the results of Jones and co-workers<sup>33</sup> are typical of those obtained by Swiss<sup>34</sup> and British<sup>35</sup> workers.

To summarize, it was found that a 10 per cent. D.D.T. powder on an inert diluent rubbed into underwear at the rate of about one ounce per person prevented infestation by lice for periods of about three weeks.



In practice, the application of such a D.D.T. dust with a hand-dusting appliance beneath the clothing of fully clothed people has been found adequate. In their studies, Bushland and co-workers exposed lice to cloth pads dusted with the 10 per cent. D.D.T. powder and found that freshly-fed lice succumbed rather less quickly than hungry lice. Freshly-fed lice were immobilized in six hours and dead within twenty hours and it was found that although not all hungry lice were knocked down after exposure for three and a half hours, the parasites no longer had the desire to feed. When a 10 per cent. D.D.T.-pyrophyllite dust was exposed to an atmosphere at 60° C. in an open vessel there was no noticeable loss of insecticidal activity after two months but after ten months' storage under these conditions, about half the toxicity was lost. In another experiment, it was shown that when garments had been dusted with a 10 per cent. D.D.T. powder and then washed once in warm soapy water the garments remained effective against lice but were not effective after a second washing.

The physical and chemical properties of D.D.T. permitted the development of impregnated clothing as an additional method of protection against insects such as lice and fleas. The method of impregnation of underwear carried out by the Allies on a large scale during the war involved the process employed in dry-cleaning. Shirts or shirting were impregnated with a solution of 5 per cent. D.D.T. in white spirit to retain about 1 per cent. D.D.T. on the weight of material. These garments were reported to be still effective in killing lice after five to eight washings.<sup>35</sup> In fact, it has been demonstrated that a D.D.T. content as low as 0.1 per cent. renders the textile effective against lice. The garments were re-impregnated in the field laundries when the content fell below the required limit, using an emulsion of D.D.T. with water as the diluent.

Details have been made available<sup>36</sup> of the results in the U.S. of experiments on the impregnation of underwear to control body lice. The practice in the U.S. Services during the war was to impregnate underwear with a 2 per cent. D.D.T. content on the weight of the garment.

Many articles, some of them decidedly not of a technical nature, have referred to the typhus epidemic in Naples. There is no doubt, however,



that the spread of typhus in Naples towards the end of 1943 was halted much more quickly than ever before in the history of medicine when D.D.T. powder was used.<sup>37</sup> Working in six groups, allied medical officers carried out case-finding, contact and special decontamination, and mass decontamination involving the delousing of about two and a half million individuals in a few months. The diagram below is of considerable interest to illustrate the course of the epidemic<sup>41</sup>:

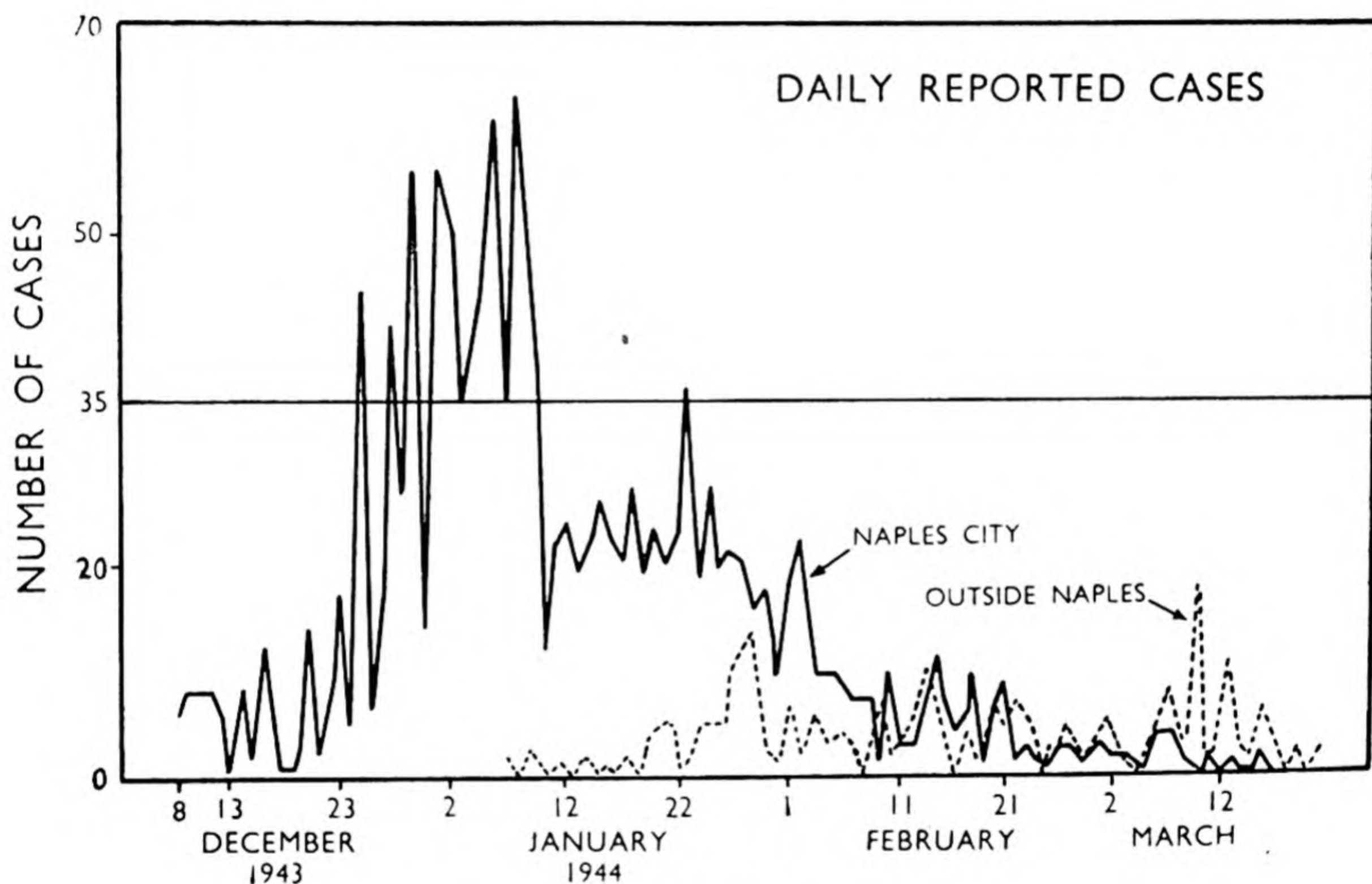


Fig. 42

It transpired that there were about 140 cases of typhus in the Buchenwald camp after liberation by the Allied army<sup>38</sup> and spread of the disease was arrested by the use of D.D.T. powder.

**Crab lice.**—A 10 per cent. D.D.T. pyrophyllite powder has been shown effective<sup>33</sup> against crab or pubic lice (*Phthirus pubis*). Application of a 10 per cent. D.D.T. powder killed the lice present at the time of treatment and the infestation was eradicated by a second



treatment eight to ten days later. No incidence of dermatitis was reported in the 100 cases of the tests.

**Head lice.**—D.D.T. dusts have also been shown effective in controlling head lice (*Pediculus humanus capitus*).<sup>39</sup> Scobbie<sup>40</sup> carried out precise laboratory experiments followed by clinical trials to compare a number of substances recommended for the destruction of head lice and nits. One application of a 2 per cent. D.D.T. emulsion cured every case treated and gave protection from reinfestation for fourteen to eighteen days with unwashed hair and from eleven to fifteen days when the hair was washed. Burn<sup>41</sup> reported that over one thousand children had been treated safely and with success for infestation of head lice with an emulsion containing 2.5 per cent. D.D.T. and no adverse effects were observed.

Eddy<sup>42</sup> has described the use of an emulsion containing both D.D.T. and benzyl benzoate as a combination treatment for head lice, crab lice and scabies (caused by *Sarcoptes scabiei hominis*). In this connection, attention is drawn to the admirable review on scabies by Gordon.<sup>43</sup> Great success has followed the use of benzoate emulsions in treating infestations on humans. Hellier<sup>44</sup> has shown that the wearing of D.D.T.-impregnated clothing and the use of D.D.T. powder did not afford protection against scabies.

**Household pests.**—Reports from various workers<sup>45</sup> show that treatment of premises with D.D.T. dusts and sprays has given consistently good results against flies, bedbugs, silver fish, ants (*Formica* spp.) but that less satisfactory results were obtained against cockroaches, cheese mites and tropical rat mites.

**Termites.**—Dews and Morrill reported<sup>46</sup> that posts can be protected from attack by termites by applying a 5 per cent. solution of D.D.T. in kerosene to the soil as the holes for the posts are refilled.

**Rat fleas.**—Simmons<sup>47</sup> has described the use of D.D.T. in controlling murine typhus. It was found that D.D.T. dust properly applied will reduce the population of fleas (*Xenopsylla cheopis*) of rats more than 95 per cent. shortly after treatment and even after months the average reduction may be as much as 75 per cent. In addition, experiments with combinations of D.D.T. with rodenticides to rid premises of both parasites and hosts were giving some degree of encouragement.



**Sandflies.**—Hertig and Fisher<sup>48</sup> reported laboratory tests in which D.D.T. gave complete kill of sandflies (*Phlebotomus* sp.)—the carrier of kala-azar and other *Leishmania*.

As a result of field trials, they recommended the spraying with a 5 per cent. solution in kerosene, of inner walls, doors, windows, screens and as much of the ceiling as possible. The outside of openings in buildings and a foot or two of the surrounding wall should also be sprayed. When shelters and breeding-places of sandflies are near buildings, outside spraying gives good control.

Simmons and Arnold<sup>49</sup> reported that painting a 5 per cent. D.D.T. solution in No. 10 motor oil on the screens of windows and doors gave some degree of control of sandflies. As the flies are attracted to lights, the walls and ceilings around the lights should also be sprayed.

**Tsetse fly.**—It has been shown<sup>50,51</sup> in laboratory tests that tsetse flies are susceptible to D.D.T. The field experiments of Symes<sup>52</sup> in Entebbe, however, illustrate the difficulties which are encountered in applying insecticides and the problems which must be overcome before effective control methods can be evolved.

**Livestock pests.**—Annand<sup>53</sup> has reviewed recently the results obtained with D.D.T. against various pests on livestock. He adds the caution that the use of D.D.T. in oil on animals is considered hazardous because some of the toxicant may be absorbed by the animal. Good control of hornflies for two to three weeks was obtained when D.D.T. (emulsions or wettable powders) was applied at the rate of 2 grams of D.D.T. per animal or by using emulsions containing 0.2 per cent. D.D.T. as a spray or a dip. A fine oil emulsion containing 0.8 per cent. D.D.T. when applied to horses infested with the winter tick killed those ticks that had attached prior to treatment and two thorough applications throughout the season prevented attachments of this species of tick.

It was found that all the motile forms of the short-nosed louse and the red louse were destroyed when cattle were immersed in a dip containing only 0.08 per cent. D.D.T. but that a concentration of 0.15 per cent. of D.D.T. was required to kill all the motile forms of the long-nosed louse and the capillate louse. There was no evidence that louse eggs were killed but the residue left in the hair killed the young lice hatching during the four to five days following the treatment and a



second dipping sixteen days after the first eliminated the infestation. Goats were also rendered free from lice by dipping in a D.D.T. bath.

Recent work has shown that the dipping of sheep in D.D.T. dips gave excellent protection against sheep blowfly (mainly *Lucilia sericata*). Cragg<sup>54</sup> found that the insecticide acts upon the adult fly whereas the arsenic-sulphur dip is larvicidal. The action of D.D.T. in the fleece was sufficiently rapid to prevent normal oviposition whereas normal egg batches were seen two days after treatment with the commercial arsenic-sulphur dip. Lyle-Stewart<sup>55</sup> confirmed that D.D.T. sheep dips appeared to be very efficacious and showed the insecticide toxic to blow-fly maggots and sheep keds (*Melophagus ovinus*).

Although promising results have been reported in Switzerland<sup>34,6</sup> with D.D.T. insecticides against European ox-warble fly (*Hypoderma bovis*) the results by workers in the U.S. have proved disappointing. Thus Stewart<sup>56</sup> reported that D.D.T. insecticides were ineffective against larvae of the ox-warbles (*Hypoderma lineata* and *Hypoderma bovis*) and Matthyse<sup>57</sup> found that there was no decrease in the grub population by applying D.D.T. sprays to legs and undersides of the bodies of cattle before turning them out to pasture.

The spraying of stables and buildings used to house animals with D.D.T. to leave a residual film has been shown to lead to great reductions in the fly population.<sup>58</sup>

Powders containing 5 to 10 per cent. of D.D.T. have been found very effective in controlling lice and fleas on farm and domestic animals and on poultry.<sup>6</sup> It has been observed that the washing of dogs with soap containing 5 per cent. of D.D.T. appeared to keep dogs free of fleas and lice for a few weeks although only minute quantities of the insecticide were present in the treated hair (about five to seven parts in ten thousand parts of hair).<sup>59</sup>

### Horticulture and Agriculture

The control of pests attacking plants appears to have been among the first experiments carried out by the Swiss workers. It was found that a small proportion of D.D.T. mixed with an inert base, such as talc, provided an effective and durable insecticide. In 1939, the potato crop



of Switzerland was threatened by an outbreak of Colorado beetle infestation and this provided the first opportunity for a large-scale trial of D.D.T. It has been stated<sup>60</sup> that the firm of J. R. Geigy, S.A., of Basle, made available to the Swiss entomologist, Dr. R. Wieseemann, a material under the name Experiment G.1750 (later known as Gesarol) and he carried out experiments in the Swiss Federal Experimental Agricultural Station at Wädenswill, confirming the Geigy results. When used in the field, the material gave very satisfactory control of the outbreak. Thus when D.D.T. was brought to the notice of the authorities in Britain and other countries towards the end of 1942, it had already been accepted in Switzerland—in the form of dusts and emulsions—as effective in controlling Colorado beetle, flea beetle, cabbage caterpillar, leek moth, onion fly, raspberry beetle and a number of other pests. Naturally, however, it was essential to test D.D.T. under British and American conditions, for instance, against the many pests attacking plants.

It is not yet possible to attempt a detailed assessment of the horticultural and agricultural uses of D.D.T. The results obtained in various countries by the many workers against a wide range of insects have been summarized recently<sup>61</sup> and other excellent summaries have recently been made available.<sup>14,53</sup>

An insecticide must be examined in trials over a number of successive seasons and under a variety of conditions and environments before it is possible to generalize on its use.

It is natural that the main research effort in D.D.T. during the war was concentrated on its use against insect vectors of diseases such as the mosquito and the louse and data were collated from competent observers all over the world. In other fields, the results published are, in some cases, rather incomplete and small areas in one locality are used as test plots. Thus it is not surprising that the results recorded by various workers are sometimes conflicting. In this sphere of application the extremely wide range of insects against which D.D.T. is effective is a source of embarrassment. Wigglesworth<sup>62</sup> has discussed the possible effects of the extensive use of D.D.T. on the balance of nature in forests, fields and streams. The so-called insect predators are insects which destroy other insects and devour them and, again, other parasitic insects deposit their eggs within the bodies of the host insect so that the



young which develop consume them. This process (natural control) of maintaining a balance in the populations of various species of insect has been utilized artificially. Thus in some cases where a harmful insect was gaining the upper hand and rendering a given crop uneconomic, insect parasites or predators have been introduced to attack the pest. These beneficial insects are, under normal conditions, a permanent method of steady control and any interference with these conditions is followed by a rapid increase in the population of the particular pest which is the prey of the beneficial insect. In developing this theme, Wigglesworth pointed out that in general, insect pests on farm crops tend to be a good deal less severe in Britain than in the United States and that the chief reason for this difference resides in the better facilities afforded to beneficial insects and birds in preying upon the pests.

Generally speaking, fields in Britain are small and surrounded by hedgerows which provide harbourage for the beneficial insects and birds and the crops are changed in rotation each year. On the other hand, in the United States large areas growing the same crop, in some cases for a period of years, provide the insect pests with the environment and opportunity for development. So far as orchard pests are concerned interesting cases have arisen already. For instance, when D.D.T. was sprayed on peach-trees to kill the Oriental moth caterpillar, the insecticide was found to be even more effective in destroying the parasite liberated as a biological method of controlling the pest than in killing the pest insects. D.D.T. is not very effective against woolly aphis but it is effective against the *Aphelinus* parasite which preys upon the former. It has been noticed, therefore, that the spraying of orchards with D.D.T. has in some cases led to an increase in woolly aphis as a by-product. Similarly, in some districts spraying of D.D.T. insecticides has been followed by a significant increase in the population of the red spider—this mite is particularly resistant to D.D.T. Naturally the effect of D.D.T. on honey bees was considered early in the work with D.D.T. in view of their importance in pollination. This aspect was observed both in Switzerland and in Germany and is still receiving close attention in this country, the United States and elsewhere. It is established beyond doubt that bees are killed by direct spraying or dusting with D.D.T. insecticides. On the other hand, contact with a dried spray film does



not appear so dangerous. The action of the dust may be due to the fact that the bees rub the particles against the sensitive parts of the body or that it acts directly upon the nerve-endings of the respiratory system. At all events, the advice given in Switzerland was to ensure that fully opened blossom was not dusted and that spraying was carried out in the evening or early morning before the bees were about.<sup>60</sup> There have been a number of papers on this subject but in general the statement of Steer<sup>63</sup> in 1945 appears to have been realized in practice.

Steer pointed out that apples, which tend to receive more insecticide treatment than other fruit, are sprayed just prior to and just following blossoming. In the special cases where conditions required treatment of trees with open blossom few bees would remain sufficiently long to be wetted by the spray. The two spray treatments involve lime sulphur as a constituent of the spray and since lime sulphur is reported to be repellent to bees this is an additional safeguard. In addition, Steer stated that in his experience, the only blossom to which insecticides are applied deliberately is that of raspberry and loganberry to control the raspberry beetles and in this case control can be effected by treatment after blossoming. In fact, while any good contact insecticide may be capable of destroying bees the proportion killed in actual practice is usually low. The risk of bees collecting "D.D.T. poisoned" pollen to feed the brood in the hive was regarded as not great. It was considered unlikely that D.D.T. would prove more harmful than such widely used materials as derris and arsenical sprays. Steer pointed out that with regard to the residual action such processes as weathering and attenuation by growth should leave little reason for undue alarm.

After consideration of the data available in 1946, the following conclusions, which were reached by an official of the Ministry of Supply<sup>14</sup> remain an excellent statement of the position with D.D.T.:

1. D.D.T. appears to be effective against almost all the common pests attacking potatoes and its use has no adverse effect on the plants or the crop.
2. It is also effective against almost all tomato pests, but there is evidence that it stunts the growth of the plants and reduces yield.
3. It is effective against many cotton pests and attacks some



insects which are difficult to control with other insecticides (*e.g.* pink bollworm). It does not control the bollweevil.

4. It will control most varieties of scale insect, leaf-eating caterpillars and thrips.

5. It controls a large number of fruit pests but its use in orchards requires great care since it is toxic to bees and attacks a number of predators and parasites of fruit pests.

6. It should not be used against pests on cucurbits.

In general, D.D.T. appears to have little phytotoxic action on most plants but cucurbits have been observed to be adversely affected and in some districts of the United States tomato plants appeared to have been affected.

It must be emphasized that D.D.T. is effective both as a contact and as a stomach poison. The contact action of D.D.T. can be illustrated by considering the results with the housefly. When flies come into contact with D.D.T. they display excitement for a short period, then a progressive paralysis slowly sets in which first affects the rear legs and then the others. It is difficult for the insects to walk straight although they are able to fly for a considerable period after this partial paralysis. Then the insects fly in an uncertain manner and finally turn over on their backs making convulsive movements with the legs and finally die. The Swiss workers considered that flies make contact with a D.D.T. deposit through the sensorial organs on the ends of the tarsi (feet) by walking over the deposit. Paralysis then commences and the poison gradually affects the whole of the nervous system. An example of the stomach poisoning action of D.D.T. is the effect on the May beetle which can swallow arsenates without being unduly affected. When these insects consume foliage sprayed with D.D.T. the nerves which operate the mandibles and digestive tracts become paralysed so that the insect is no longer able to feed and death follows starvation or breakdown of the nervous system.

Annand<sup>53</sup> has reviewed the extensive experiments carried out by investigators of the U.S. Bureau of Entomology and Plant Quarantine and summarized the conclusions as follows:



1. If the insecticide containing D.D.T. can be successfully mixed and used with fungicides, it will serve as an excellent remedy for several widespread pests of potatoes, such as the Colorado beetle, the potato leafhopper, the potato psyllid, and possibly aphids affecting potatoes.

2. If the residue hazard is found to be negligible, it should serve as a remedy for caterpillars on cabbage in areas where the cabbage aphid or turnip aphid is not a problem.

3. On tomatoes in California D.D.T. will probably prove to be the most effective remedy yet found for the tomato fruitworm.

4. On peas it can be used as a satisfactory treatment for the pea weevil and probably for the pea aphid.

5. On squash, pumpkins, melons and other cucurbits its use will be limited because of its adverse effect upon these plants; it is ineffective against the melon aphid.

6. On sugar beets grown for seed, unless some unforeseen difficulty arises, present indications are that a 5 per cent. D.D.T. dust will be a standard remedy for *Lygus* and other types of plant bugs which attack seed beets. It may also be useful against the beet leafhopper under certain conditions.

7. For the market gardener who grows different types of vegetables and who has the Mexican bean beetle to contend with, D.D.T. will not be a satisfactory all-purpose insecticide; a combination of rotenone and pyrethrum will probably be more effective.

In aerosol form, D.D.T. will probably find its greatest usefulness in the control of plant lice, such as the pea aphid and aphids that attack potatoes. Preliminary work has shown the D.D.T. aerosols to be effective initially against other insects, but their residual value has not been determined. D.D.T. in aerosol form should also provide a convenient and effective method of controlling many of the pests that are found in the greenhouse.

It is convenient to conclude this brief discussion of the use of D.D.T.



in agriculture and horticulture with a copy of a press notice (January, 1946) by the Ministry of Agriculture and Fisheries:

“The discovery of the powerful insecticidal properties of the chemical known as D.D.T. (dichloro-diphenyl-trichloroethane) has aroused great public interest. It proved of the greatest value in the control of lice, bugs, mosquitoes and other insects affecting the health and comfort of the allied armies, and, during the war, almost the whole output of this material was required for military uses. Now it has become available for use in agriculture and horticulture, and it is important that this valuable new material should be employed to the best advantage.

“The chemical D.D.T. is not a finished insecticide; it needs to be compounded for use in the form of dusts or for application as a wet spray in the form of suspensions or emulsions. Experimental work indicates that insecticides containing small quantities of D.D.T., suitably prepared and properly applied, will kill a wide range of insect pests affecting our crops including, for example, cabbage caterpillars, flea beetles, and apple blossom weevil. On the other hand, for some pests, such as ‘greenfly’, D.D.T. seems to be less effective or no better than insecticides at present in use; and on some others, for example, red spider, it has little or no action. When more is known of the best way in which to use them, D.D.T. insecticides may prove of value for the control of pests against which at present they do not seem to be promising; but however that may be, the fact that D.D.T. is so generally toxic to insects raises certain problems in connection with its agricultural uses.

“Fears have been expressed that, if D.D.T. is widely used, bees and other pollinating insects and also parasites and predators of insect pests may be killed on a sufficient scale to neutralize the good done by destruction of pests and that the ‘balance of nature’ may be upset. D.D.T. insecticides can undoubtedly kill beneficial insects, but so can many insecticides in common use and this is no new problem. Most insecticides, if widely and indiscriminately employed, would be likely to cause harm in greater or lesser degree by destroying beneficial insects but, in practice, properly applied on the scale normal in this country, it is found that there is little to fear in this respect. The disturbance of nature’s balance is local and temporary, and the value of the crops saved



by the appropriate use of insecticides far outweighs this disadvantage. Special care may be necessary with D.D.T. because of its persistent qualities, but there is no good reason to expect that adverse results will follow if D.D.T. insecticides are employed sensibly and with the same precautions and on the same kind of scale on which other insecticides are used. One precaution that should certainly be taken with D.D.T. as well as with other insecticides is to avoid applying them to fruit trees when in blossom.

“D.D.T. is less poisonous to man and animals than some insecticides at present in use. Nevertheless, ordinary precautions of a kind already familiar to users of insecticides, such as avoidance of undue exposure and the prevention of contamination of foodstuffs, should be taken. At the normal strengths in which D.D.T. is used in sprays and dusts, it has been found harmless to human beings and livestock.

“Although a great deal of experimental work has been done in the past year or two, it is only very recently that sufficient quantities of D.D.T. have been available for field experiments on pests of farm and garden crops, and for this reason it has not yet been possible to obtain full information about its possibilities and the best methods of using it for various purposes. Every effort is being made to fill the gaps in our knowledge, but experimental work of this kind inevitably takes time. Farmers, fruit-growers and gardeners who intend to try D.D.T. insecticides should, in the meantime, regard them as experimental and use them with due care until there has been time for entomologists and chemists to ascertain in more detail how they can be most efficiently and safely employed. We have in D.D.T. a chemical that shows great promise of being a most valuable addition to the means available for control of many insect pests of crops, and so for increasing food production, and it would be particularly unfortunate if it should be wrongly used in the early stages of its development.”

Martin and Wain<sup>64</sup> pointed out that as D.D.T. is relatively non-poisonous it has a wider scope than lead arsenate and, when sufficient data is available, may be preferred for spraying food crops near harvesting or where vegetable undercrops are preferred. A combined D.D.T.-lime sulphur spray would also avoid the lead sulphide sludge inherent in lead arsenate lime sulphur. Although D.D.T. appears to be



without fungicidal properties it appears to be compatible with fungicides such as lime sulphur and Bordeaux mixture.

**Forest insects.**—Craighead and Brown<sup>65</sup> have recently summarized D.D.T. investigations for controlling forest insects with special reference to aerial application. Extensive tests were carried out for the control of forest pests such as the spruce budworm, gypsy moth, hemlock looper, pine-tip moths, spittle bugs, pine sawflies, and white-pine weevil. The experiments were designed to obtain information on minimum dosages required to give effective control, to compare D.D.T. formulation, to improve equipment for releasing sprays from aircraft, and to study the effects of D.D.T. on other forms of animal life in the areas treated. D.D.T. appeared to be very effective for controlling a number of forest pests at a concentration of  $\frac{1}{8}$  to  $\frac{1}{4}$  lb. to the acre. These authors considered that much more work was needed with emulsions and suspensions to study their efficacy as compared with that of oil solutions. Suspensions appeared to be less injurious to aquatic life and as they formed larger droplets less material was lost in application from the air. It was considered that solving of many mechanical problems on aircraft spraying equipment, etc., would be necessary before it was possible to take full advantage of the low dosage requirements and residual effect of D.D.T. and at the same time avoid danger to fish and wild life. Cottam and Higgins<sup>27</sup> have reviewed the data on the effect of D.D.T. on fish and wild life and gave the following recommendations for minimizing the danger:

“Use D.D.T. for the control of an insect only after weighing the value of such control against the harm that will be done to beneficial forms of life. Wherever more than a small area is involved, consult country agricultural agents, State or Federal entomologists, wild-life and fishery biologists and United States Public Health Service officials.

“Use one-fifth of pound or less D.D.T. per acre in an oil solution to avoid damage to fishes, crabs or crayfishes; use less than two pounds per acre to avoid damage to birds, amphibians, and mammals in forest areas. Because of its greater effectiveness, use smaller quantities of D.D.T. in emulsion.

“Use D.D.T. only where it is needed. Wherever it is applied by



airplane, provide careful plane-to-ground control to ensure even coverage and to prevent local overdosage.

“In forest pest control, wherever feasible, leave strips untreated at the first application to serve as undisturbed sanctuaries for wild life, treating these strips at a later time or in succeeding seasons if necessary.

“In the control of early appearing insect pests, apply D.D.T., if possible, just before the emergence of leaves and the main spring migration of birds; for late appearing pests, delay application, whenever practicable, past the nesting period of birds. Adjust crop application and mosquito-control applications so far as possible to avoid the nesting period.

“Because of the sensitivity of fishes and crabs to D.D.T., avoid as far as possible direct application to streams, lakes and coastal bays.

“Wherever D.D.T. is used, make careful before-and-after observations of mammals, birds, fishes and other wild life.”

### Benzene hexachloride

According to Slade,<sup>66</sup> in the course of tests in the I.C.I. laboratories during 1942, a sample of hexachlorocyclohexane (synonyms: benzene hexachloride,  $C_6H_6Cl_6$  or “666”) was found to be promising against the turnip flea beetle. The sample examined was prepared in 1942 by chlorinating benzene in the presence of light and crystallizing the product from benzene. Although the results of laboratory and small-scale field trials in the summer of 1942 were promising, they were not so consistent as was to be expected.

It was found later that these inconsistencies could be attributed to varying proportions of isomers in the benzene hexachloride mixture. As early as 1912<sup>67</sup> Van der Linden had succeeded in isolating four isomers from the mixture obtained by chlorinating benzene.

Slade<sup>66</sup> discussed the complex stereochemical\* consideration involved

\* Stereochemical, spatial configuration of a compound as affected by isomerism— isomers being compounds having the same empirical formula but different molecular structure.



in the possible configurations for benzene hexachloride. It was decided that although sixteen possible configurations are possible for the hexachloride only five are probably strainless forms; of these, two are mirror images. The four isomers in the pure state were described<sup>66</sup> as colourless, crystalline compounds, practically insoluble in water, soluble in organic solvents, practically inodorous and possessing bitter tastes. The melting points of the isomers were given as follows:

Alpha	( $\alpha$ )	m.p. 157.5 — 158° C.
Beta	( $\beta$ )	m.p. 309° C.
Gamma	( $\gamma$ )	m.p. 112.5° C.
Delta	( $\delta$ )	m.p. 138 — 139° C.

The I.C.I. workers found that the  $\gamma$ -isomer showed extraordinary insecticidal properties whilst the  $\alpha$ -,  $\beta$ - and  $\delta$ -isomers had feeble insecticidal properties.

Kauer, Duvall and Alquist<sup>68</sup> have reported recently the isolation of a fifth isomer (epsilon isomer) from the mixture of isomeric forms of benzene hexachloride. This epsilon isomer was present in small amounts and appeared to possess little insecticidal activity. It had m.p. 218.5 — 219.3° C. and the infra-red absorption data and X-ray powder diffraction patterns showed it to be different from the four isomers isolated previously.

According to Bourne<sup>69</sup> benzene hexachloride has been used in France before and during the war under the name "Aphtiria".

### Toxicity to warm-blooded animals

Slade<sup>66</sup> reported results of Dr. H. Taylor showing that the following quantities per kgm. of body-weight were necessary to obtain a 50 per cent. kill (in seven days) of rats when introduced into the stomach.

Alpha isomer	. . . .	1.7 grammes per kgm.
Beta isomer	. . . .	No animals were killed
Gamma isomer ("Gammexane")	. . . .	0.19 grammes per kgm.
Delta isomer	. . . .	1.00 grammes per kgm.
The mixture of isomers	. . . .	1.25 grammes per kgm.



The trade name "Gammexane" was given to the gamma-isomer. Rats were fed 10, 20 or 30 mg. of "Gammexane" per day for five weeks without effects of any kind being produced and 100 mg. of the mixture of isomers was fed daily with the food for two months to rats without producing any effect.

No ill effects followed the painting of the tails and ears of rats with a 5 per cent. emulsion twice daily for a fortnight.

Subcutaneous injection of 100 mg. of "Gammexane" killed 25 per cent. of the rats and the rest were severely affected but recovered in three days. No effect was produced when 600 mg. of the mixed isomers per kgm. were injected.

Goldfish were unaffected by saturated aqueous solutions of the alpha and beta isomers (the alpha isomer was found to dissolve to the extent of about ten parts per million in distilled water and the beta isomer about five parts per million parts of water). The delta isomer affected the fish slightly at concentrations of ten to twelve parts per million and the gamma isomer was distinctly toxic to fish at a concentration of one part per million.

### Formulation

Slade<sup>66</sup> has stated that as a substitute for derris powder a finely divided powder containing 20 per cent. of crude benzene hexachloride and 80 per cent. gypsum was prepared and this powder was further diluted with selected materials to give insecticidal powders for use on crops. When required in solution, solvents such as xylene, carbon tetrachloride, perchloroethylene and decahydronaphthalene were used. Such solutions containing high percentages of "Gammexane" are dilutable for use with kerosene or other suitable oil.

The addition of an emulsifying agent such as Turkey red oil to these solutions gave products which could be diluted to provide dilute emulsion for use on crops.

Wettable or dispersible powders containing "Gammexane" could be produced by incorporating a proportion of "Goulac" (this is a waste lye arising during the sulphite treatment of cellulose).

The fact that "Gammexane" is stable at high temperatures was



stated to permit its dispersal by such means as volatilization from hot plates.

### Mode of Action

In discussing the mode of action, Slade<sup>66</sup> pointed out that "Gammexane" has the properties of killing by contact action, as a stomach poison and as a fumigant. The isomers of benzene hexachloride are more volatile than D.D.T.—thus the former are capable of acting as fumigants but naturally give a less persistent residual action than D.D.T. It was found, for instance, that "Gammexane" can exert a lethal fumigant action at room temperature against grain weevils. As an example of the contact action German cockroaches dusted with mixtures containing benzene hexachloride isomers showed excitement within a few minutes, followed by the onset of convulsions in twenty to forty minutes and death in a few hours. When houseflies were sprayed with solutions of the insecticide, knockdown of the insects was less rapid than with pyrethrum but convulsions were produced within a few minutes, followed eventually by death. The stomach poison action was shown, for instance, in tests against the locust hoppers which were killed after feeding on baits containing one part of the mixture of isomers (the crude product contained 10 to 12 per cent. gamma-isomer) to 2,000 parts of bran.

Slade<sup>66</sup> drew attention to the fact that in spite of the great advance in medicine we still know little concerning the mode of action of chemotherapeutic agents upon the life processes of the cell. We quote an account of the development of an extremely interesting theory to explain the mode of action of gamma-benzene hexachloride from Dr. Slade's paper published in *Chemistry and Industry*.

"The control of life processes has not yet emerged from empiricism and can only do so as our knowledge of biochemistry expands. However, we have a few guiding principles which have emerged from recent work and these should help us to introduce some plan into the testing of chemicals *in vivo*. One of these principles has emerged from the empirical discovery of the sulphonamide drugs, namely, that the active



chemotherapeutic agent masquerades as a molecule which is essential for the life of a cell. In other words, *p*-amino-benzene sulphonamide reacts where *p*-amino-benzoic acid should have been in a normal cell reaction, but is then unable to perform the next function of normal cell life. So the cell dies.

“ We know quite a lot about the chemical structure of the constituents of cells, *e.g.* amino acids, sugars, porphyrins, fats, nucleotides, etc., but we cannot always point out with certainty which of these metabolites are essential to the life process. We can only try empirically.

“ Now inositol is a metabolite which is found widespread in many types of cells and thus we would infer from our masquerading hypothesis that if we could lock up a molecule which would be similar to it, not only in molecular dimensions, but also in some physical prerequisites, then it should be taken up by an organism and gain general access to its cells. Benzene hexachloride isomers are molecularly similar to inositol, and ‘ Gammexane ’, on this hypothesis, very similar indeed. Thus it is possible that ‘ Gammexane ’ is absorbed from the outside of the insect, distributed throughout some portion of the organism to the cells where a vital reaction is blocked, and the organism dies.

“ The specificity of physiological action demonstrated by the separate isomers is of interest and this fact should be borne in mind when considering the action of D.D.T. The latter compound may also be blocking the vital reaction which is dependent upon inositol but it must be remembered that D.D.T. seems to have only one-fifth to one-fifteenth the power of ‘ Gammexane ’ against certain insects, and it may be, therefore, blocking quite a separate vital reaction. All this is very speculative, but I believe that compounds of highly specific physiological potency will be found to be of great value for the chemical investigation of vital processes in the cell.”

Kirkwood and Phillips<sup>70</sup> reported that turbidity measurements showed that  $\gamma$ -hexachlorocyclohexane inhibited the growth of a yeast requiring exogenous inositol. Furthermore, the inhibition was reversible by adding sufficient *iso* inositol to the treated culture. It had been shown by the original workers that the  $\alpha$ -,  $\beta$ - and  $\delta$ -isomers had little insecticidal activity and it was found that these compounds produced only slight growth inhibition of the yeast and this was not reversible by



adding inositol. This supports the suggestion that the insecticidal action of the  $\gamma$ -isomer is due to interference with insects' inositol metabolism. This interference was thought to be due to similarity in the spatial configuration of  $\gamma$ -hexachlorocyclohexane and the *isoinositol*. Buston and co-workers<sup>71</sup> have published, independently, results supporting the work of Kirkwood and Phillips.

### Insecticidal properties

Slade<sup>66</sup> gave the following figures for the toxicity of the isomers of benzene hexachloride to the grain weevil:

TABLE 10

<i>Relative toxicity of the isomers of benzene hexachloride to the grain weevil (Calandra granaria) when applied as grain dust.</i> By H. H. S. BOVINGDON	
Test substance	Relative amounts by weight to give 50 per cent. kill in five days in each case
Alpha isomer .. .. .	900
Beta isomer .. .. .	Almost non-toxic
Gamma ("Gammexane") .. .. .	1
Delta isomer .. .. .	5,500
An effective "inert" dust of the alumina type .. .. .	6,600
D.D.T. .. .. .	15

The actual amount of "Gammexane" required to give 50 per cent. kill in five days was 0.4 per cent. per million of the weight of the grain.

Data for the toxicity of solutions in odourless distillate were given as follows:



TABLE 11

*Toxicity of the isomers of benzene hexachloride when used in solution in odourless distillate as spray against the housefly.*

By H. H. S. BOVINGDON

Test substance	Concentration of spray per cent. w/w	Mortality per cent.
Alpha isomer .. .. "Gammexane" .. ..	0.8 (saturation) 0.01	21.00 73.0
Delta isomer .. .. D.D.T. .. ..	1.1 (saturation) 0.02	24.0 51.0

Slade gave the following list of insects and other pests killed by 'Gammexane':

TABLE 12

*Insects and other pests killed by "Gammexane"*

INSECTA	
<i>Orthoptera</i>	African migratory locust, <i>Locusta migratoria migratorioides</i> (R. and F.). House cricket, <i>Gryllulus domesticus</i> (L). German cockroach, <i>Blatella germanica</i> (L). Oriental cockroach, <i>Blatta orientalis</i> (L).
<i>Anopleura</i>	Body louse, <i>Pediculus humanus</i> (L).
<i>Hemiptera</i>	Bed-bug, <i>Cimex lectularius</i> (L).
<i>Lepidoptera</i>	Various leaf-eating larvae, e.g.: Cabbage caterpillars, <i>Pieris</i> spp. Winter moth caterpillars, <i>Cheimatobia brumata</i> (L). Clothes moth caterpillars, <i>Tineola bisselliella</i> (Hüm.). Melon worm, <i>Diaphania hyaliniata</i> (L). Southern armyworm, <i>Laphygma eridana</i> (Cram.). Southern beet webworm, <i>Pachyzancla bipunctalis</i> (F).
<i>Coleoptera</i>	Various flea beetles, <i>Phyllotreta</i> spp. Mustard beetle, <i>Phaedon cochleariae</i> (F). Blossom beetle, <i>Meligethes aeneus</i> (F). Apple blossom weevil, <i>Anthonomus pomorum</i> (L). Pea and bean weevil, <i>Sitones lineatus</i> (L). Grain weevil, <i>Calandra granaria</i> (L). Hide beetle, <i>Dermestes vulpinus</i> (F).

[contd.]



TABLE 12—continued

INSECTA—contd.	
<i>Hymenoptera</i>	Wasps, e.g. <i>Vespidae</i> spp. Ants, e.g. <i>Lasius</i> spp.
<i>Diptera</i>	Various mosquitoes, e.g. <i>Aedes aegypti</i> (L) (adults and larvae). <i>Anopheles gambiae</i> Giles, <i>A. maculipennis</i> Meigan, <i>Theobaldia</i> , spp., etc.
<i>Aphaniptera</i>	Housefly, <i>Musca domestica</i> (L). Various fleas, e.g. <i>Otenocephalus</i> spp.
ARACHNIDA	Poultry red mite, <i>Dermanyssus gallinae</i> (De Geer).
CRUSTACEA	Woodlice, <i>Oniscidae</i> spp.

Bishopp<sup>72</sup> has recently reviewed the work carried out with benzene hexachloride by the U.S. Bureau of Entomology and Plant Quarantine and stated that there was considerable variation in the benzene hexachloride products tested so that a lack of uniformity in the results was to be expected. One disadvantage was that the material had a persistent musty odour and although material now being supplied was less objectionable in odour it would be necessary to produce benzene hexachloride with less odour before it could be used for some purposes. According to Bishopp, benzene hexachloride was somewhat disagreeable to work with especially in dust form and appeared to be highly toxic to honey-bees. The material appeared to exhibit a fumigant action but since it was more volatile than D.D.T. it was less persistent. As Bishopp pointed out, from the point of view of harvested crops this might be an advantage.

Benzene hexachloride was found very effective against both the adult houseflies and larvae and although as a residual spray the duration of efficacy of the treated surface was briefer than with D.D.T., the knock-down of the yellow fever mosquito (*Aedes aegypti*) was found to be more rapid. The insecticide was found effective against body lice (and appeared to exert some ovicidal action) and against cattle lice and cattle grubs and preliminary results showed it was valuable in controlling the black-legged tick, the lone star tick and the chigger. In agriculture, promising results had been obtaining against the cotton boll weevil, the



cotton aphid and thrips on cotton, the cotton flea hopper, tarnished plant bug, lygus bugs, stink bugs, the red spider on cotton, white fringe beetle, tobacco thrips on peanuts, vetch brucid on hairy vetch, sugarcane borer, corn flea beetle and corn earworm on corn. Tests against



**Fig. 43.**—The untreated area on the right shows devastation caused by wireworm. The left-hand side has been treated with benzene hexachloride. *Photograph by courtesy of Plant Protection Ltd.*

grasshoppers with benzene hexachloride applied as a dust, a spray or in baits had shown erratic results in the hands of U.S. workers. Benzene hexachloride showed some toxicity to the Mexican bean beetle and was effective against the green peach aphid on potatoes in some tests but a condition resembling leaf-mould followed its use. It appeared to be less effective than D.D.T. against the pea aphid and was not highly



effective against codling moth when used as a spray at the rate of 0.2 to 0.5 lb. of gamma isomer per 100 gallons (U.S.) of spray. As a soil treatment for the control of Japanese beetle grubs benzene hexachloride appeared to be effective in dosages as low as  $\frac{1}{4}$  to  $\frac{1}{2}$  lb. of gamma isomer per acre.

Bishopp observed that oats, rice and cowpeas show some injury if grown on soil in which the top three inches had been treated at the rate of 5 lb. or more of gamma isomer per acre and since a number of varieties of young plants showed leaf burn when treated with benzene hexachloride at concentrations of 0.1 per cent. or more care was necessary in using the material. He considered that further study was essential to determine the toxicity of benzene hexachloride to warm-blooded animals, the hazard involved in residues on crops, and it was necessary to find a means of eliminating the musty odour and flavour imparted to food products.

When used as a residual spray against the elm bark beetle, carrier of Dutch elm disease, benzene hexachloride inhibited feeding for thirty-eight days as compared with sixty-six days for D.D.T. of similar strength. Benzene hexachloride appeared to be more effective than D.D.T. in protecting logs and timber from attack by the ambrosia beetle and was certainly more effective than dichlorodiphenyloxide which is usually recommended for this purpose.

Steward<sup>73</sup> has reviewed the preliminary results in the application of "Gammexane" to arthropods of veterinary importance. It would appear that "Gammexane" is showing great promise against several genera of ticks and Steward concluded: "Among the synthetic insecticides 'Gammexane' is outstanding in acaricidal activity, and this important veterinary use is being investigated further."

It must be emphasized that a number of these insecticides are in their infancy and much work will be necessary before a clear picture can emerge. Thus as a result of tests in New Zealand, Taylor<sup>74</sup> summarized his results as follows:

"Slade (1945) recorded that the insecticidal action of '666' is due almost entirely to the gamma isomer and suggested that its toxicity is approximately five times that of D.D.T., *i.e.* that two parts crude '666' (containing 10 per cent. gamma isomer) are equivalent to one part of



D.D.T. These calculations appear to have been based either on laboratory trials or under conditions where residues were not subjected to weathering. The trials here recorded show that under field conditions '666' failed to give a similar toxicity ratio to D.D.T., with the exception of the trial against carrot-aphid.

"The failure of '666' to maintain toxicity against grass-grub beetle after sixteen days' weathering suggests that as a protective insecticide it is not likely to be as effective as D.D.T. Support is given to this view by the failure of '666' at twice the dosage rate of D.D.T. to give comparable control of white butterfly. Against codling moth equal dosage rates showed marked inferiority in control by '666'. On the other hand, '666' proved highly efficient in control of carrot-aphid results suggesting that less than two parts of '666' are of equivalent toxicity to one of D.D.T. against this pest, *i.e.* that the gamma isomer of '666' may be more than five times as toxic as D.D.T.

"Results of red-mite control are interesting in that populations of mites showed increase on '666' plots, but not to the same extent as on those sprayed with D.D.T. It appears probable that both D.D.T. and '666' were non-toxic to the mites, but by killing predacious insects, allowed rapid increase in populations of red mite."

### Chlordane

A recent development is the discovery<sup>75</sup> of a new synthetic insecticide having the empirical formula  $C_{10}H_6Cl_8$  which was referred to in early reports as "1068" but which is now generally referred to as "Chlordane".

This material has not yet been fully described chemically but is probably a mixture of isomers not yet resolved and evaluated individually. The compound has remarkable insecticidal properties and in the United States it is already finding extensive use chiefly in products to control household pests such as cockroaches, against which it is remarkably effective.

**Physical properties.**—"1068" when purified by vacuum distillation (boiling point  $175^\circ$  at 2 mm. pressure) is a viscous, colourless, odourless liquid. This sample was regarded as at least 99 per cent.



pure and according to Kearns and co-workers<sup>75</sup> showed no tendency to be irritating to the skin or mucous membranes. The compound "1068" is soluble in all proportions in most organic solvents such as aromatic, aliphatic and chlorinated hydrocarbons, ketones, ethers and alcohols but is insoluble in water. This solubility is of considerable importance in the formulation of insecticides containing the material. Like D.D.T. and "Gammexane", "1068" has the property of dehydrodehalogenation in the presence of alkaline reagents to form a product which is substantially non-toxic to insects. It is of low volatility and appears to be somewhat less volatile than "Gammexane" but more so than D.D.T. This means that under comparable conditions "1068" provides a residual effect longer than that obtainable with "Gammexane" but of shorter duration than with D.D.T.

"1068" can be made into insecticidal compositions for use as oil solutions, emulsions, dusts and wettable powders.

**Insecticidal properties.**—Kearns, Ingle and Metcalf<sup>75</sup> summarized their results as follows:

"A series of parallel tests were made on '1068' and D.D.T. applied as aqueous dispersions to the *spiraea* aphid and to the pea aphid (*Macrosiphum pisi*). The results of these tests indicated that '1068' is several times more toxic to these insects than is D.D.T. and that the pea aphid is the least susceptible of the two species to both compounds. Aqueous sprays of '1068' and D.D.T. applied to potato foliage and later infested with third and fourth instar larvae of the Colorado potato beetle likewise showed '1068' to be more toxic than D.D.T. to this insect. The two compounds applied to the adult squash bug in the form of aqueous sprays and as dusts revealed D.D.T. to be relatively ineffective as compared with '1068'."

The residual toxicity of "1068", D.D.T. and  $\gamma$ -benzene hexachloride was compared by applying emulsified xylene solutions of the compounds to the surface of wall-boards, which were then exposed at intervals over a period of sixteen weeks to adult *Anopheles quadrimaculatus*. The increase in time required to produce a 100 per cent knockdown as the treated surfaces aged was used as an index of loss in effectiveness of the compounds, by volatilization, absorption or other means. After fifteen weeks of ageing, the time required for  $\gamma$ -benzene hexachloride treatment to produce a 100 per cent. knockdown had increased by a factor of ten over its initial knockdown time. In the same period, the time required for the "1068" treatment to produce a 100 per cent.



knockdown had increased by a factor of 3, whereas, that of D.D.T. remained approximately constant. It would seem that of the three materials, D.D.T. will produce the most permanent toxic surface. It is believed that the loss in residue effect from "1068" and  $\gamma$ -benzene hexachloride is due to their greater volatility, the latter being the more volatile of the two. Preliminary volatility measurements indicate "1068" to be considerably more volatile than D.D.T.

A series of tests made to compare the larvicidal properties of "1068", D.D.T. and  $\gamma$ -benzene hexachloride to the larvae *Anopheles quadrimaculatus* resulted in the conclusion that there was no significant difference in the three compounds when applied as acetone suspensions, emulsions and dusts.

The relative toxicity of "1068" and D.D.T. to the adult housefly was measured by the "large group" Peet Grady procedure. Under the conditions of the tests, it was found that 0.2 per cent. D.D.T. or 0.05 per cent. solutions of "1068" are required to produce a 95 per cent. mortality in twenty-four hours. A median lethal concentration was estimated from probit-log dosage curves which indicated that 0.06 per cent. solution of D.D.T. or an 0.02 per cent. solution of "1068" would be required. The relative toxicity of "1068" and D.D.T. to the American roach was determined by applying precisely measured dosages to the thoracic tergites. Dosage mortality curves plotted from data obtained in these tests showed "1068" to be approximately three times as toxic as D.D.T. to this insect. The median lethal dose for "1068" was found to be approximately 14 micrograms per gram of body weight as compared to 38 micrograms per gram of body weight for D.D.T., when measured 120 hours after treatment. The corresponding values for LD 95 were approximately 25 micrograms per gram of body weight for "1068" and 70 micrograms for D.D.T. per gram of body weight.

Stomach poison tests with "1068", D.D.T. and  $\gamma$ -benzene hexachloride were made on the adult grasshopper (*Melanoplus differentialis*). Emulsions of xylene solutions of the active compounds were fed to the grasshoppers in measured drops. Twenty-four-hour mortality records indicated the median lethal dosage for  $\gamma$ -benzene hexachloride to lie between 5 and 10 micrograms, for "1068" between 12.5 and 25



micrograms, and for D.D.T. to be greater than 50 micrograms per gram of body weight.

Bishopp<sup>76</sup> has reported the results of preliminary tests carried out in laboratories in the U.S. Bureau of Entomology and Plant Quarantine with "1068". Works at Orlando, Florida, found that against larvae of the malaria mosquito the toxicity of "1068" was practically identical with that of D.D.T. (0.1 p.p.m. killed 98.3 per cent. in each case in twenty-four hours). The "1068" was found to display outstanding efficacy against the body louse but appeared to be less persistent than D.D.T. or "3956". Powders containing "1068" as an active ingredient were found to be more toxic to the German cockroach than D.D.T. However, in preliminary laboratory tests, these workers found the material to be less toxic than D.D.T. to the armyworm, celery leaf tier and variegated cutworm. At a concentration of 10 per cent. the "1068" was more toxic to the pea aphid than 1 per cent. of nicotine and 2 per cent. of "1068" appeared to be less toxic to this insect than 1 per cent. of the gamma isomer of benzene hexachloride. When sprays containing 5 to 20 ml. of "1068" per gal. (U.S.) of water were applied at the rate of 1 gal. per sq. yard there was a complete kill of larvae of the Japanese beetle. The "1068" showed promise against the tarnished plant bug on cotton and lygus bugs on alfalfa. It was found that 90 to 100 per cent. of the grasshoppers in alfalfa plots were killed by applying "1068" as a dust or spray at the rate of 1 lb. to the acre and furthermore the insecticide retained its killing properties for at least two weeks. When an emulsion containing "1068" was applied to corn ears, the results were promising against the corn earworm and when using a wettable powder containing "1068" a good residual action effect was obtained against the confused flour beetle.

Since this manuscript was prepared it has been stated<sup>77</sup> the name "Chlordane" has been coined by the U.S. Bureau of Entomology and Plant Quarantine for the chlorinated hydrocarbon  $C_{10}H_6Cl_8$ . It was stated to be 1, 2, 4, 5, 6, 7, 8, 8-octachloro-4, 7-methano-3a, 4, 7, 7a-tetrahydroindane.

#### **Toxaphene (3956)**

Recently, Bishopp<sup>78</sup> has reported the results of tests in the U.S. with



another chlorinated persistent insecticide to which the code name "3956" had been applied. According to another report,<sup>2</sup> "3956" is a chlorinated camphene manufactured by the Hercules Powder Company and the trade name "Toxaphene" has been adopted. Bishopp<sup>78</sup> stated that "3956" displayed an action similar to that of D.D.T., viz. slow knockdown and kill and providing a persistent toxic effect on sprayed surfaces. These preliminary tests showed that "3956" appeared to be less effective than D.D.T. against houseflies as a contact spray, in aerosols and as a spray residue. It was also somewhat less effective against adult yellow fever mosquitoes. Outstanding results had, however, been shown against the body louse and against this pest "3956" was even more toxic and more persistent than D.D.T. Household pests such as cockroaches, bedbugs and carpet beetles were also stated to be susceptible to the insecticide. As with D.D.T., it is necessary where a quick knockdown action against household insects is desired to include a proportion of pyrethrum or one of the organic thiocyanates in the spray.

In preliminary laboratory tests<sup>78</sup> the material was reported to have shown considerable toxicity to the southern armyworm, certain cutworms, the celery leaf tier, some boll weevils, bollworms, tarnished plant bugs and cotton aphids, grasshoppers, European corn borer larvae, corn earworm and sugarcane borer. In one test an application of a spray containing 1 lb. of "3956" to 100 gallons (U.S.) of water was found to reduce the population of orchard mites by 98 per cent.

Stearns<sup>79</sup> has reported that "3956" is a light yellow, waxy product with a very mild pine odour, melting point 65 to 90° C. and has excellent solubility in common organic solvents. It has the empirical formula  $C_{10}H_{10}Cl_8$  and contains 67 to 69 per cent. chlorine.

Stearns<sup>79</sup> found that normal storage conditions had no appreciable effect upon the toxicity of "3956" and summarized his results as follows:

"The performance of the chlorinated bicyclic terpene (3956) in the case of certain household insects approximates that of D.D.T. Both chemicals are relatively slow-acting; both exhibit a high kill at low concentrations, and both display a marked residual effect. Synthetic '3956' and D.D.T. sprays proved equally and highly toxic to the house-



fly. When compared as residual toxicants over a twelvemonth period, complete kills of this species were effected by both compounds in essentially the same time. Used as a spray against the German cockroach, '3956' was superior to D.D.T. at all concentrations except five per cent.; at that rate, both of them killed 100 per cent. of the test insects. Dust formulations of '3956' (10 per cent.) were likewise successful. Highly satisfactory results were obtained with the black carpet beetle, the furniture carpet beetle, and the webbing clothes moth. However, certain dry-cleaning fluids, as applied to the treated fabrics, rendered '3956' partially to wholly ineffective by simple solvent extraction. A high mortality was recorded when '3956' was used in direct and in residual sprays against the bed bug."

Naturally much more work will be necessary before it is possible to assess the relative value of "3956" and other compounds of this group.

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## CHAPTER XV

### REPELLENTS AND ATTRACTANTS

DURING the war when allied troops were fighting throughout the world often under conditions unsuitable for the white man, it was essential to develop methods of rendering the environment as acceptable as possible. The investigation of substances capable of protecting people from the bites of insect disease vectors was therefore greatly intensified. It is essential to distinguish between the use of insecticides (to kill insects) and repellents. The latter are usually applied to the skin or to clothing or fabric to discourage mosquitoes or other insects from approaching and biting. In some cases, the repellent may also possess insecticidal properties, *e.g.* pyrethrum, but this is not essential. For instance, dimethyl phthalate is an excellent repellent but has little insecticidal action. The subject of repellents, with special reference to mosquitoes, has been dealt with recently by Christophers<sup>1</sup> who considered, however, that repellent action was, as a rule, fairly general in effect against biting insects although some degree of specificity was displayed by certain repellents against different insects.

In 1916, Howard regarded spirits of camphor, oil of pennyroyal and oil of citronella as among the best of these remedies. For instance, a mixture of oil of citronella, 1 ounce, spirits of camphor, 1 ounce, and oil of cedarwood,  $\frac{1}{2}$  ounce, was recommended. Covell<sup>2</sup> mentions that Dover's pomade was widely used in India in 1941 and had been adopted by the armed forces in a slightly modified form. The formula given for Dover's preparation is as follows, oil of citronella,  $\frac{1}{2}$  ounce, spirits of camphor,  $\frac{1}{4}$  ounce, cedarwood oil,  $\frac{1}{4}$  ounce, white petroleum base, 2 ounces. Other methods such as the burning of pyrethrum flowers or the volatilization of phenols have been used to kill and prevent mosquitoes from entering a room. Antimosquito sprays are used for the same purpose and according to Covell, when these sprays (which usually contain pyrethrum extract dissolved in kerosene) are sprayed over the ankles and socks there is a repellent effect for a considerable period. Other substances which have been recommended are sulphur,



bergamot oil, oil of thyme, oil of cassia, spruce oil, oil of lime, oil of turpentine and oil of tar. In the period between the two world wars, pyrethrum preparations had been examined and found effective as repellents. For instance, Ginsburg<sup>3</sup> reported that the spraying of an aqueous pyrethrum preparation when applied to grass, bushes, etc., provided considerable protection from mosquito annoyance for several hours at outdoor gatherings.

For personal application, however, Christophers<sup>1</sup> reported that pyrethrum, though an excellent insecticide, was less efficient as a repellent. It has been found<sup>1</sup> that repellents do not behave exactly alike in their manner of exerting repellency. Thus dimethyl phthalate repels at a much shorter distance than citronella oil which tends to drive the mosquitoes away. The mechanism by which the various substances repel insects is not known but some sense-organ must be involved. There is little doubt that the great impetus given to research on repellents during the war will be followed up to seek an explanation for the phenomenon of repellence.

A large number of compounds were tested at the Orlando laboratory of the U.S. Bureau of Entomology and Plant Quarantine<sup>4</sup> and as a result of this work and that of Christophers' dimethyl phthalate, indalone ( $\alpha$ ,  $\alpha'$ -dimethyl- $\alpha'$ -carbobutoxy- $\gamma$ -dihydropyrone) and 2-ethylhexanediol-1,3 were used alone and in combination to protect Service personnel during the war.<sup>5</sup>

One of the most interesting chemicals developed recently for personal use is 2-ethyl-hexanediol-1, 3 (known as insect repellent No. 612 or as Rutgers 612). Granett and Haynes<sup>6</sup> have described the discovery of the repellent properties at Rutgers University and subsequent development by Government Agencies during the war. It is a slightly viscous, colourless liquid with a very faint odour and does not affect by solvent action cellulose acetate, cellulose nitrate, or polystyrene but rapidly softens shellac. The commercial material has the following specification, maximum acidity as acetic acid 0.01, specific gravity at 20° C. 0.9390 to 0.9430, boiling range 240 to 250° C. Granett and Haynes carried out a series of comparisons with dimethyl phthalate against various species of mosquitoes and summarized their results and those of other workers in Table 13:



TABLE 13

*Repellent tests against various species of mosquitoes, 1942 to 1945.*

Location of tests	Species	2-ethyl -hexanediol-1, 3		Dimethyl Phthalate	
		No. of tests	Protec- tion time	No. of tests	Protec- tion time
Rutgers Laboratory	<i>Aedes aegypti</i> ..	60	Mins. 536	29	Mins. 455
New Jersey Salt Marshes .. Reported in U.S. Patent No. 2,356,801 Travis & Jones, Aug. 29th, 1944 ..	<i>Anopheles</i> <i>quadrimaculatus</i>	4	60	5	123
	<i>Aedes sollicitans</i> and <i>Aedes cantator</i>	19	352	6	233
	<i>Aedes aegypti</i> ..	—	363	—	234
	<i>Anopheles</i> <i>quadrimaculatus</i>	—	78	—	206
	<i>Aedes</i> <i>tachiorhynchus</i> ..	—	276	—	153
Tests in Panama .. Kumm & Jobbins	<i>Anopheles</i> <i>albimanus</i> ..	40	157	—	103
		—	230	—	90
Tests in South Pacific, Travis ..	<i>Anopheles</i> <i>punctulatus</i> ..	—	350	—	40

In these tests, measured quantities of the chemicals were applied to a given surface area of skin (usually 1 mil. to 100 square inches) and exposed the treated surface to hungry mosquitoes taking the time from application to the first bite as the protection time. The tests were conducted at 75° F. and 50 to 60 per cent. relative humidity. It was found in the case of both ethylhexanediol and dimethyl phthalate that a definite increase in the time of repellency was observed as more repellent was applied although the effectiveness was not directly proportional to the quantity used. When diluents were added to the repellents, the repellency was found in general to be a function of the concentration of active ingredient in the mixture. Granett and Haynes<sup>6</sup> pointed out that the results obtained in practice were usually of shorter duration due to such factors as excessive perspiration, mechanical removal of repellent



variation in absorption by the skin in different areas and the difficulty of providing uniform coverage especially on the face and head—protection being given only where the repellent is applied. Thus in the field against salt marsh mosquitoes (*Aedes sollicitans*) ethylhexanediol was found to give protection from two and a half to four and a half hours while dimethyl phthlate was effective for two to two and a half hours. It has been estimated that about 40 per cent. of the bites received during exposure to mosquitoes under natural conditions take place through clothing at points where these are in contact with the body. Granett and Haynes found that when slack suits were impregnated with 20 per cent. by weight of repellents biting from salt marsh mosquitoes was prevented for up to eight days using ethylhexanediol and for about two days with dimethyl phthalate. These suits were worn during half of each working day for the test period. Rain appeared to remove the repellents from the cloth and reduced the effectiveness of the impregnation treatment.

The results of repellency tests carried out by these workers with other pests are summarized in Table 14.

In addition, tests carried out at the Orlando laboratory of the U.S. Bureau of Entomology and Plant Quarantine showed that while not completely effective, ethylhexanediol did give protection against bedbugs (*Cimex lectularius*). Against the Southern buffalo gnat (*Eusimulium pecuarum*) an average of 508 minutes' protection was obtained by applying ethylhexanediol to five men and an average of 330 minutes' protection after application to domestic animals. Granett and Haynes<sup>6</sup> considered that "extensive toxicological studies and large-scale use by the armed forces have indicated its safety and lack of irritant properties". (It is obvious that any compound which is to be applied to the skin must be examined most carefully for possible adverse effects.)

One of the mixtures most widely used during the war was the so-called 6-2-2 mixture or 60-20-20 mixture consisting of 60 per cent. dimethyl phthalate, 20 per cent. ethylhexanediol (Rutgers 612) and 20 per cent. indalone, and Jones, McCollough and Morton<sup>7</sup> have studied the effect of storage on this and other mixtures.

During the war, outbreaks of scrub typhus (later recognized as tsutsugamushi disease) necessitated urgent action. Lewthwaite<sup>8</sup> has



TABLE 14

*Repellent tests against arthropod pests other than mosquitoes.*

Test species	Ethyl Hexanediol		Dimethyl Phthalate	
	No. of tests	Protection time	No. of tests	Protection time
		Mins.		Mins.
Stable fly (6) <sup>1</sup> <i>Stomoxys calcitrans</i> ..	—	101	—	47
Black fly <i>Simulium</i> spp. .. ..	6	350	—	316
Sand flies <i>Phlebotomus</i> spp. .. ..	—	240	—	240
Fleas (5) <i>Ctenocephalides canis</i> <i>C. felis</i> .. ..	32	139	28	260
Chiggers (4) <i>Eutrombicula</i> spp. <i>Acariscus maroni</i> .. ..		On treated suits 30 days	—	30 days

<sup>1</sup> Number in parenthesis indicates references cited.

reviewed the history of the control measures adopted for this disease which is carried by certain mites. It was found that more satisfactory results as a mite poison were obtained by impregnating the uniform with dibutyl phthalate than with dimethyl phthalate or D.D.T. Also, the observers considered that none of these compounds repelled mites but that they poisoned them. As a result of experiments by U.S. workers, benzyl benzoate has been recommended for the same purpose, *i.e.* impregnating clothing to prevent mites attacking the wearer.<sup>9</sup>

For some years before the war, the use of solutions of pyrethrum extract in suitable oils was advocated as a method of protecting cattle for some hours after spraying by the repellent action against flies. Synthetic insecticides have also been used for this purpose (see *e.g.* F. W. Atkeson, A. R. Borgmann, R. C. Smith and A. O. Shaw).<sup>10</sup>



Recently the properties of the so-called repellent "N.M.R.I. 448" have been described. This mixture was tested at the Naval Medical Research Institute, Bethesda, U.S.A., from which the initials are derived. This mixture, which consists of a 30/70 ratio of 2-cyclohexyl-cyclohexanol and 2-phenylcyclohexanol is claimed to be especially effective against several species of mosquitoes in tropical areas. In U.S. public service patent No. 2,396,031, Jones and Travis claim an insect repellent containing 2-phenylcyclohexanol and disclose the use of 2-cyclohexyl-cyclohexanol for insect repellent purposes. The mixture "448" is a clear, moderately viscous, non-greasy liquid and the mixture tends to solidify at about 20-28° C. The repellent properties of "448" against a series of insects using a test under tropical conditions (four drops of repellent were applied to the face or neck, four drops to each arm and six drops to each leg) are summarized by the Naval Medical Research Institute in Table 15:

TABLE 15

Species repelled	Average period (in hours) affording complete protection
<i>Aedes aegypti</i> :	
<i>A. taeniorhynchus</i> .. .. .	5
<i>A. euplocamus</i> .. .. .	5—6
<i>A. augustivittatus</i> .. .. .	10*
<i>Anopheles albimanus</i> .. .. .	11*
<i>A. darlingi</i> .. .. .	9*
<i>A. pseudopunctipennis</i> .. .. .	10*
<i>Psorophora ferox</i> .. .. .	10*
<i>Uranotaenia</i> sp. .. .. .	10*
"Bedbugs" .. .. .	12*
"Sandflies" .. .. .	4*
Mites: "Chiggers" .. .. .	8*

\* Indicates that tests were interrupted.

A formula recommended by workers in the U.S. consists of 60 per cent. "448", 38 per cent. alcohol and 2 per cent. water.

Thomssen and Doner<sup>11</sup> have drawn attention to the fact that the repellent action of pine tar oil was known as long ago as 1899 and has



been used until recently in a petroleum oil base as a repellent for flies on cattle. Such pine oil sprays tend to impart odours to milk and have been replaced by synthetic repellents such as the organic thiocyanates and phenoxychloroethyl ether.

The application of a mixture of benzol and diphenylamine to the wounds of livestock has been found to destroy screw worm larvae and to repel the adults thereby preventing further infestation. The sheep maggot fly (*Lucilia sericata*) was found to be repelled by olive oil, cotton-seed oil and oleic acid.

No correlation has yet been found between the chemical constitution and physical properties of repellents; a substance that is pleasant to a human being may have quite the opposite effect on insects.

### Attractants

Thomssen and Doner<sup>12</sup> have reviewed the results and experiments carried out in the use of attract ants in traps and baits.

Traps containing a mixture of geraniol and engenol are used to attract Japanese beetles and about 25,000 lb. of geraniol is used annually in the United States for this purpose.

A mixture of cider, brown sugar, yeast and water was found an efficacious bait for the codling moth and the Oriental peach moth and in one experiment,<sup>12</sup> 17,429 codling moths were caught in 93 traps set in a six-acre orchard. Such traps for codling moth, apart from their value in helping to reduce this pest, provide a useful guide to the time when the normal lead arsenate spray should be applied. Although normal spray schedules are established, this method is sometimes used in the United States so that maximum spray results may be obtained.<sup>12</sup>

A number of materials have been tested in attempts to find more attractive codling moth baits. Of those tested, the methyl series of phenyl, acetic, malonic, propionic and oxalic acid esters and the ethyl series of malonic, propionic and oxalic acid esters were significantly attractive. Later experiments showed that the phenyl derivatives of the lower organic acids, alcohols and esters showed better attractant properties than their parent compounds.

Experiments using attractants against other insects showed that



tobacco hornworm moths are attracted to certain amyl esters of salicylic acid; baits of fish meal on sticky fly-papers attract carpet beetles and clothes moths. Casein, gelatin, bakers' yeast, filter press mud, cow-hide with hair attached, cow blood, egg white, wheat shorts, certain amino acids and proteins in the presence of sodium hydroxide solution have been shown to be attractive to the Central American fruit fly (*Anastrepha striata*). It has also been demonstrated that proteins are attractive to the apple fruit fly (*Rhagoletis pomonella*). Thomssen and Doner concluded that a great deal of work remains to be done in this field before this phase of control of insects can be utilized to the best advantage.

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## CHAPTER XVI

### WEED CONTROL

WEEDS invariably appear wherever man cultivates the soil, either for crops or ornamental purposes. Weeds compete with crops for water, light and the mineral nutriment of the soil, and greatly reduce yields whilst at the same time increase labour costs by adding to the difficulties of such operations as “singling” and harvesting. In addition, they provide shelter for insect pests and in some cases act as alternative host plants which form centres of infestation. The direct loss to the crop by the action of weeds may be as much as 50 per cent.<sup>1</sup> and the elimination of these undesirable plants forms one of the major agricultural problems of to-day.

Whilst some weed killers have been known for many years, it is only recently that intensive study of their economic possibilities has been made, stimulated in part by the discovery of the selective action by certain chemicals and growth-regulating substances.

Non-selective weed killers are employed where it is desired to free ground from all vegetation, as, for instance, railway tracks, aerodromes and pathways. Robbins and co-workers<sup>2</sup> have discussed the chemicals which can accomplish this and have listed among them—sodium arsenite, sodium chlorate, unrefined petroleum oils, sodium dichromate, sodium and potassium bisulphate, zinc chloride, zinc sulphate and sodium ethyl xanthate.

Of more interest are the selective weed killers which possess lethal properties only to certain species of plants and therefore can, by careful selection, be used to eliminate some weeds while leaving the main economic crop unharmed. For the moment, this is only practicable in the elimination of broad-leaved weeds growing in monocotyledonous crops, but certain experiments indicate there is also the possibility of producing the reverse effect. The use of the older inorganic weed killers such as iron sulphate, the copper salts and sulphuric acid have been admirably dealt with by Robbins *et al.*,<sup>2</sup> Long and Brenchley<sup>1</sup> and



we shall confine ourselves to brief notes on the newer organic preparations.

Ripper<sup>3</sup> and Black<sup>4</sup> have reported that sodium dinitro *ortho* cresol has given good results in the elimination of weeds in cereal and flax crops, but it has the disadvantage of being inflammable. This material, under the trade name of "Sinox" was developed in France in 1933, and has been used commercially in California. Dinitro *ortho* cresol is not inflammable and experiments have indicated that it is superior in action to the sodium salt and when used with the addition of the ammonium salts it proved more selective and killed a wider range of weeds.

The most recent development in weed control has been the utilization of "growth regulators" or synthetic plant hormones. These chemicals are able to stimulate in some plants certain physiological changes which usually are the normal responses to naturally occurring hormones developed within the plant itself; thus both *alphanaphthylacetic* acid and *indolacetic* acid will stimulate root formation in some herbaceous plants while applications of *betanaphthoxyacetic* acid to tomato flowers will induce fruit formation even if no fertilization has taken place. Growth regulators are specific in their action inasmuch as any particular chemical affects only a limited number of species or variety of plants and the concentrations used to obtain these reactions are very low, being only a few parts per million. If greater concentrations are used they bring about distortions in plant growth which may eventually lead to death.

Advantage has been taken of the specificity of growth regulators, coupled with their lethal properties in the greater concentrations, to use them as selective weed killers. So far, they have been used chiefly for weed control in cereal crops, for monocotyledons, as a class, have proved resistant to their action.

In the United States, the most widely used growth regulator as a selective weed killer is 2, 4 dichlorophenoxyacetic acid which is extremely active. As little as 1-2 parts per million will induce the formation of tomato fruits from unfertilized flowers while at 100 parts per million, undesirable distortions in growth appear;<sup>5</sup> at 1,000 parts per million, those plants sensitive to this chemical are killed. Cereals and grasses are resistant.





**Fig. 44.**—Corn treated with "Agroxone," on the right the untreated corn is practically submerged by yellow charlock. *Photograph by courtesy of Plant Protection Ltd.*



2, 4 dichlorophenoxyacetic acid, known as D.C.P.A. or 2, 4-D, is insoluble in water and is therefore applied either as a dust in an inert carrier or as water emulsion using a suitable solvent and emulsifier. D.C.P.A. will readily form salts and of these the sodium and ammonium and triethanolamine compounds are soluble in water and may therefore be applied as a solution thus eliminating the necessity of using emulsions. Harvey<sup>6</sup> lists some fifty species of weeds that are susceptible to D.C.P.A. and twenty-three which are resistant; he recommends applications at the rate of  $\frac{3}{4}$  to 3 pounds per acre, according to the species of weed it is desired to eliminate, but concludes that as our knowledge of this growth regulator is still limited, considerable care should be exercised in its use.

D.C.P.A. is absorbed by the plant either through the leaves or through its roots; although its action is not fully understood, the lethal effect is concerned with disturbances to the growth mechanism resulting in abnormal development and contortion. It has been recommended that a concentration of 0.1 per cent. of D.C.P.A. may be considered as the standard strength and that when applied as a spray there should be sufficient quantity of liquid to wet the weed leaves;<sup>7</sup> the best results are obtained when the weeds are in the seedling stage or in active growth for the mature and dormant stages are more resistant. D.C.P.A. is now used extensively for the elimination of weeds in cereals and grasses and has also been tried in citrus groves where cultivation of the soil is not practised.

In Great Britain, research on similar lines has led to the development of 4-chloro-2-methylphenoxyacetic acid as a selective weed killer, chiefly for use in cereal crops. This chemical, known as Methoxone or M.C.P.A. and marketed under the name Agroxone, may be applied as a dust or as an aqueous solution and at a concentration of only 1-2 pounds per acre and is lethal to charlock, pennycress, corn buttercup and a number of other common weeds in cereals. It does not damage wheat or oats but in a few cases some malformation in barley has been observed. The mode of action of M.C.P.A. and D.C.P.A. is essentially similar and the development of the former chemical in Great Britain rather than the latter was probably due to the availability of the raw materials in the country.<sup>5</sup>



TABLE 16

*Selective control of annual weeds in cereal crops**Relative Efficiency of Different Herbicides**Concentrations of material per 100 gallons of spray solution per acre*

Weed Species	B.O.V. (sulphuric acid) gal.	Copper Chloride 16	D.N.O.C. 16	M.C.P.A. 16	D.C.P.A. 16
Yellow Charlock ..	7-10***	10-15***	6-8***	1.0***	1.0***
Pennycress ..	7***	15***	4-6***	0.75***	(1.0)***
Treacle Mustard ..	10***	20***	5-7***	1.5***	(1.5)***
White Charlock ..	13**	20-30**	8**	2.0***	2.0***
Corn Buttercup ..	13*	R	8*	2.0***	2.0***
Shepherd's Needle	15*	R	8*	2.0***	2.0***
Corn Poppies ..	R	R	6-8W***	2.0*	(2.0)*
Fat Hen ..	12W**	R	6-8***	2.0*	(2.0)*
Goosefoot or Orache	12W**	R	6-8***	2.0*	(2.0)*
Mayweeds ..	13W*	R	6-8***	R	R
Camomile ..	13W*	R	6-8***	R	R
Corn Marigold ..	13W*	R	8W***	R	R
Cleavers ..	10***	20-30*	6-8**	R	R
Knotgrass ..	13W***	R	8*	R	R
Willow Weed ..	13W**	20-30*	8*	R	R
Hemp Nettle ..	10***	20-30**	6-8***	(2.0)**	?
Annual Nettle ..	10W***	(R)	6-8**	(2.0)*	?
Spurrey ..	10***	20*	6-8W**	2.0*	?
Speedwell ..	10***	20**	6-8**	R	?
Bearbind ..	10***	20-30***	6-8**	2.0*	2.0*
Chickweed ..	13**	R	8*	R	R
Cornflower ..	(13W)*	R	(8W)**	(2.0)***	?
Parsley Piert ..	(13W)***	R	(5-7)***	R	?
Fumitory ..	R	R	6-8W***	R	(R)
Shepherds' Purse ..	10W***	(30)**	7**	(2.0)*	?

\*\*\* = Over 90 per cent. kill expected; \*\* = Over 80 per cent.; \* = Over 50 per cent.

R = Weed resistant.

() = Figures are tentative.

? = Information not yet available.

Although the development of the growth-regulator type of selective weed killer marks a considerable advance in weed control, those which have so far been discovered are far from perfect. They do not kill all the common weeds while, at the same time, great care must be taken in



their application to ensure that they do not drift into fields of root and vegetable crops or flowers where they can cause extensive damage. In order to secure weed elimination in any one area, it is necessary first to study the weed association and then to select the appropriate selective killer according to the predominant weed. Blackman,<sup>8</sup> who has extensively studied this problem, has published a table (table 16, opposite) showing the relative efficiency of the different selective herbicides now available.

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